SYNTHETIC TANNINS

Synthetic Tannins

THEIR SYNTHESIS, INDUSTRIAL PRODUCTION AND APPLICATION

BY

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AUTHOR'S PREFACE

WHILST the synthesis of the natural tannins has been successfully outlined by Emil Fischer, it has been left to the Chemical Industry, notably the Badische Anilin und Soda-fabrik in Ludwigshafen-on-the-Rhine, to discover the means of making possible the production of the synthetic tannins.

The scientific results of Fischer's researches are to-day common knowledge, and these, together with questions arising therefrom, will only be lightly touched upon in the book herewith presented. Even an attempt at enumerating the present synthetic tannins has so far not been published, and I have therefore availed myself of the opportunity of making a brief summary of them. My work at the B.A.S.F. deepened my insight in this new field; ample opportunity of applying these synthetic products in practice was given me when, as a result of the war, I was appointed technical consultant to the Austrian Hide and Leather Commission, and in this capacity was called upon to act as general adviser to the trade. The ultimate object of my scientific researches was then to investigate the chemistry of this particular field, and this has led me to present a picture, complete as far as it goes, of this branch of chemical technology.

The intention of the present volume is to communicate to the reader what has so far been scientifically evolved and practically applied in this field. First of all, however, it may illustrate the extreme importance and the universal applicability of the synthetic tannins in the making of

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leather. The modern leather industry cannot, to-day, be without these important products; but also in those tanneries, where the synthetic tannins have not so far been regarded as indispensable, their use is strongly recommended. Just as in the case of the coal-tar dyes, the synthetic tannins will make us independent of foreign supplies, and thus keep within our own borders the vast sum of money required in former days for the purchase of foreign tanning materials. May this book prove the means of providing an incentive for a still wider application of the synthetic tannins.

GRASSER.

GRAZ, *August* 1920.

TRANSLATOR'S PREFACE

)OCTOR GRASSER hardly needs an introduction to the
:ather trade of this country in its scientific aspect, but if
ne be sought for, none could serve the purpose better than
translation of the book herewith presented to the British-
)eaking public.

Viewed with curiosity from their start, the synthetic
nnins needed—like many other important discoveries—an
:treme emergency for the purpose of showing their value.
he Great War provided the opportunity of which chemical
dustry was to avail itself, and to-day we do not only see
nthetic tannins placed upon the market as a veritable
iumph of chemical technology and a creditable triumph of
anufacturing chemistry; we also see their immensely
actical qualities established as a fact, and, as the author
tly remarks, no modern tanner can to-day dissociate him-
lf from the use of synthetic tannins for the production of
ither in the true sense of this word. There is no branch of
ither-making where synthetic tannins cannot help and
prove processes already established.

The immense number of substances patented by German
anufacturing chemists for the purpose of producing synthetic
ining materials is almost staggering. In view of this fact
is doubly pleasing to see that British chemists have found
w ways, and are able to produce equally good and more
ied synthetic tannins than has hitherto been deemed
ssible. The originator of these products and his acolytes

must at least share the credit with those who, in spite of the limitations necessarily set by the former, have been able to find new and better ways.

In his book Dr Grasser gives a short review of the necessary forerunner of any work upon synthetic tannins: the investigations and syntheses of the natural tannins. It is certainly to be hoped that we may soon see such works as those of Fischer's and Freudenberg's, recently published, translated into English. For the guidance of the reader it may be noted that a short account of the works of these authors may be found in the *Journal of the Society of Leather Trades' Chemists*, vol. v. (May issue); in addition to this, some of the matter contained in the chapter on synthesis of tanning matters appeared in the January 1921 issue of the *Journal of the American Leather Chemists' Association*.

In addition to these two sections, the last part of this book deals with the practical application of synthetic tannins, and it is hoped that the tanner will find much valuable information in these pages. The main outlines of the syntheses of tanning matters should prove of great value to the chemist engaged in this branch of chemical technology.

The translator takes great pleasure in acknowledging the valuable assistance rendered him by Mr Robin Bruce Croad, A.R.T.C., F.I.C., and by Mr Arthur Harvey.

<div align="right">F. G. A. ENNA.</div>

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INTRODUCTION

CLASSIFICATION OF SYNTHETIC TANNINS

N laying down a definition of "Synthetic Tannins," it is
rst of all necessary to clearly define the conception of
tannin." Primarily, tannins may be considered those
ibstances of vegetable origin which may be found, as water-
oluble bodies, in many plants, exhibiting certain chemical
ehaviour, possessing astringent properties and being capable
f converting animal hide into leather. This latter property
f the tannins, that of converting the easily decomposable
rotein of animal hide into a permanently conserved substance
id imparting to this well-defined and technically valuable
roperties, has become the criterion of the practical con-
deration of a tannin. It appears that different substances
ertainly show the chemical reactions peculiar to the tannins,
id to a certain extent also exhibit astringent character
ithout, however, possessing the important property peculiar
 the tannins of converting hide into leather. Such
ibstances, in our present-day terminology, are termed
seudo-tannins (e.g., the "tannin" contained in coffee-beans).
ecomposition products of the natural tannins, to which
elong, for instance, gallic acid and the dihydroxybenzenes,
:hibit the well-known reactions of the tannins (coloration
ith iron salts), but they cannot be regarded as tannins from
ther a technical or a physiological standpoint.

As regards their chemical constitution, the natural (true)
nnins probably belong to different groups of organic
ompounds, and with our present-day scant knowledge of
eir chemistry, it is impossible to classify them. One is,
owever, justified in assuming that both the natural tannins
id the related humic acids are ester-derivatives of hydroxy-
enzoic acids.[1]

The production of synthetic tannins employs two quite

[1] E. Fischer, *Ber.*, 1913, 46, 3253.

distinct methods ; one is to synthesise the most simple tannin, viz., the tannic acid contained in galls (tannin), or to build up substances similar in character to the tannins, from hydroxy-benzoic acids. The other, entirely new way, is to produce chemical substances, which certainly have nothing in common with the constitution of the natural tannins, but which behave like true tannins in contact with animal pelt, and in addition, since they can be manufactured on a commercial scale, are of practical value.

Owing to the fact that, until recently, the constitution of tannin has remained unknown, it is easy to comprehend that the efforts to synthesise the latter substance, or compounds similar to it, have been mainly attempted on similar lines. The oldest investigation in this direction dates from H. Schiff,[1] who pre-pared substances similar to tannin by dehydrating hydroxy-benzoic acids. By allowing phosphorus oxychloride to inter-act with phenolsulphonic acid, he obtained a well-defined substance possessing tanning properties, which he considered an esterified phenolsulphonic acid anhydride, the composition of which he determined as $HO.C_6H_4.SO_2.O.C_6H_4JISO_3$. It is, however, probable that this substance is not homogeneous, but consists of a mixture of higher condensation products.

Klepl[2] obtained—by simply heating p-hydroxybenzoic acid—a so-called di- and tridepside, but this simple method is not applicable to many other hydroxybenzoic acids, since these are decomposed by the high temperature required to induce reaction.

Amongst other attempts to produce condensation products with characteristics similar to those possessed by the tannins, those by Gerhardt[3] and Loewe[4] must be especially noted ; they treated gallic acid with phosphorus oxychloride or arsenic acid, and thereby obtained amorphous compounds, exhibiting the reactions characteristic of tanning substances. E. Fischer and Freudenberg,[5] by treating p-hydroxybenzoic

[1] Liebig's *Ann.*, 1873, 43, 170.
[2] *Jour. pr. Chem.*, 1883, 28, 208.
[3] Liebig's *Ann.*, 1853, 87, 159.
[4] *Jahresb. f. Chem.*, 1868, 559.
[5] Liebig's *Ann.*, 372, 45.

id in the same way, succeeded in obtaining a didepside,
d during the last years practically only these two
vestigators have demonstrated the syntheses of these
psides and produced high-molecular polydepsides.

At the same time researches were instituted with the
ject of determining the constitution of tannin, and E. Fischer
cceeded in demonstrating its probable composition as being
at of a glucoside containing 5 molecules of digallic acid
r 1 molecule of glucose.

This last-named class of synthetic tannins—which may be
pperly termed "tanning matters" in contradistinction to
e true tannins—exhibit very distinct tanning character
en brought in contact with animal hide, but from the
int of view of chemical constitution have nothing in
mmon with the natural tannins. Not only are they of
erest to the industry from a practical point of view; they
ve also been examined very closely from a chemical stand-
int.

It is, however, necessary to differentiate with great exacti-
le between the conception of *true tanning effect* and *pickling
ct* when considering the action of chemical substances on
t (*i.e.,* animal hide, treated with lime, depilated, and the
plus flesh removed). Whereas any *true tannage* is char-
erised by the complete penetration of the substance and
subsequent fixation by the pelt in such a way that a
rough soaking and washing will not bring about a recon-
sion (of the leather) to the pelt state; *pickling*, on the
er hand, is only characterised by the penetration of the
stance in the pelt and fixation to such an extent that a
sequent washing of the pickled pelt will bring back the
ter to a state closely approximating that of a true pelt.
ple as such a differentiation appears, there are still a
mber of cases occupying a position between the two
erred to, and which we may term *pseudo-tannage*. An
mple of the latter is formaldehyde tannage; formaldehyde
for a long time been employed in histological work for
purpose of hardening animal hide, by which it is readily
orbed from solution whereby it hardens the hide without,
vever, swelling it. A hide which has thus been treated

with formaldehyde absorbs the natural tannins with greater
ease; this, on the one hand, argues the probability of formal-
dehyde acting as a pickling agent; on the other hand, it is
also one of its characteristics that it will either in neutral
acid,[1] or, still better, in alkaline[2] solution, convert pelt into
leather.   In a formaldehyde-tanned leather, however, no
trace of tannin can be detected ; and the yield (of leather,
based on the pelt employed), which, from a practical stand-
point, is so important, is so very low that it is hardly possible
to speak of it as a tannin in the ordinary sense of the
word.   Formaldehyde must, therefore, be termed a pseudo-
tannin.

The tanning effect of formaldehyde is, according to Thuau,[3]
increased by those salts which bring about colloidal poly-
merisation of the formaldehyde, the resultant compounds
being absorbed by the hide fibre.   Fahrion considers this to
be a true tannage, and is supported by Nierenstein[4] :—

$$R.NH_2 \atop R.NH_2 \text{(Hide.)} + \underset{\text{H}}{O.C.H.} = \underset{\text{(Leather.)}}{R.NH \atop R.NH} CH_2 + H_2O$$
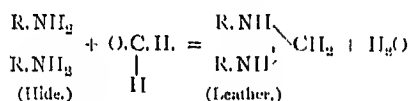
A peculiar combination between true tannage and pickling
is to be found in the tawing process (tannage with potash,
alum, and salt), whereby, firstly, the salt and the acid char-
acter of the alum produce a pickling effect, and secondly, the
alum at the same time is hydrolysed, and its dissociation
components partly adsorbed by the hide, thereby effecting
true tannage.   This double effect is still more pronounced in
the synthetic tannins which contain colloidal bodies of pro-
nounced tanning intensity on the one hand, inorganic and
organic salts on the other, which then act as described above.
Their real mode of action can only be explained with the aid
of experimental data.   The following chapters will deal with
the different behaviour of the various groups of synthetic
tannins.

[1] R. Combret, Ger. Pat., 112, 183.
[2] J. Pullman, Ger. Pat., 111,408 ; Griffith, *Lea. Tr. Rev.*, 1908.
[3] *Collegium*, 1909, 363, 211.
[4] *Ibid.*, 1905, 157, 159.

PART I

SECTION I

THE SYNTHESIS OF VEGETABLE TANNINS

1. Tannin

THE first investigations of gall-tannin date from the year 1770, at which time, however, no exact differentiation between tannin and gallic acid was made. The first step in this direction was made when Scheele,[1] in 1787, discovered gallic acid in fermented gall extract, and in the same year Kunzemüller[2] separated gallic acid (or pyrogallol) as a crystalline body from oak galls. Dizé[3] continued the investigations, which were brought to a conclusion with Deyeux' work[4]; both recognised that the substance isolated was not a single substance, but was a mixture of gallic acid, a green colouring matter, a rosin (tannin?), and extraneous matter. Proust[5] was the first to differentiate the crystalline gallic acid from the amorphous, astringent substance, which latter he named " Tannin."

Amongst the numerous subsequent investigations of tannin must be especially noted the one by Berzelius,[6] who purified the potash salt and decomposed this with sulphuric acid. Pelouze,[7] later on, observed the formation of the crystalline gallic acid from tannin, when the latter is boiled with sulphuric acid; this had already been observed by J. Liebig.[8] Both had noticed the absence of nitrogen. In addition to the methods of preparation of tannin then in vogue neutral solvents were mainly employed by subsequent investigators; Pelouze[9] treated powdered galls with ether containing alcohol and water, and considered the upper layer to be a solution of gallic acid and impurities, the bottom layer to contain the pure tannin.

[1] Grell's *Chem. Ann.*, 1787, 3, 1.
[2] *Ibid.*, 1787, 3, 413.
[3] *Jour. Chim. et Phys.*, 1791, 399.
[4] *Ann. Chim.*, 1793, 17, 1.
[5] *Ibid.*, 1799, 25, 225.

[6] Pogg, *Ann.*, 1827, 10, 257.
[7] Liebig's *Ann.*, 1843, 47, 358.
[8] *Ibid.*, 1843, 39, 100.
[9] *Jour. prakt. Chem.*, 1834, 2, 301, and 328.

The **Empirical Formula** of tannin has also been the subject of much speculation by the different investigators, the difficulty here being that of obtaining a pure specimen of the substance free from sugars, and which could be submitted to elementary analysis. Whereas these early purified substances were thought to correspond to the formula of digallic acid (galloylgallic acid), $C_{14}H_{10}O_9$, Fischer and Freudenberg[1] were able to show, with approximate certainty, that the constitution of tannin is that of a pentadigalloyl glucose.

Early attempts at *hydrolysing tannin* gave varying results, some investigators claiming the presence, and others the absence of sugars. Here, again, E. Fischer and Freudenberg[2] were able to conclusively prove that on hydrolysing tannin with dilute acids, 7.9 per cent. glucose is dissociated, and that hence glucose forms part of the tannin molecule. Fischer and Freudenberg also determined the optical activity of pure tannin in water: a_D was found to lie between $+58°$ and $+70°$.

Graham found[3] that the *tannin molecule* is of considerable size, since its diffusion velocity is 200 times less than that of common salt. Paternò[4] was the first to determine the molecular weight of tannin, employing Raoult's method ; he found that tannin in aqueous solution behaves like a colloid and that hence Raoult's method is not applicable. When, on the other hand, he dissolved tannin in acetic acid, results concordant with the formula of $C_{14}H_{10}O_9$, corresponding to a molecular weight of 322, were obtained. Sabanajew[5] later determined the molecular weight of tannin in aqueous solution as 1104, in acetic acid solution as 1113-1322, Krafft[6] as 1587-1626 in aqueous solution. Walden[7] determined the molecular weight of tannin-schuchardt as 1350-1560, tannin-merck as 753-763, digallic acid as 307-316 (calculated 322). Feist[8] determined the molecular weight of tannin as 615 and one of his own preparation as 746, Turkish tannin as 521 and Chinese tannin as 899. In this connection it should be

[1] *Ber.*, 1912, 915 and 2709.
[2] *Ibid.*
[3] *Phil. Transact.*, 1861, 183.
[4] *Zeits. phys. Chem.*, 1890, iv. 457.
[5] *Ibid.*, 1890, v. 192.
[6] *Ber.*, 1899, 32, 1613.
[7] *Ibid.*, 1898, 3167.
[8] *Chem. Ztg.*, 1908, 918.

oted that the calculated molecular weight of pentagalloyl
lucose, which in E. Fischer's opinion forms a substantial part
f the tannin molecule, is 940, but Fischer also thinks that
his compound possesses a much higher molecular weight.

Structure of Tannin.—The oldest structural formula of
annin is Schiff's digallic acid formula :— [1]
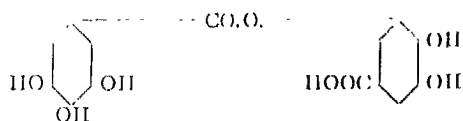
A drawback to the acceptance of this formula is the
bsence of an asymmetrical C-atom ; the formula, therefore,
oes not explain the optical activity exhibited by tannin.
chiff attempted to overcome this difficulty by adopting a
agonal structural formula, but even when adopting Clauss'
agonal formula for benzene the optical activity of a number
̂ other compounds depends upon the existence of the
symmetrical C-atom. Biginelli[2] also opposed the digallic
cid formula, and supported his view by referring to the arsenic
ompounds obtained by him on heating arsenic acid and
illic acid, instead of obtaining digallic acid. Walden,[3] on the
her hand, found, on analysing the digallic acid thus prepared,
nly slight traces of arsenic and, by the elementary analysis,
btained figures closely corresponding to those of digallic acid.

Böttinger[4] prepared the so-called β-digallic acid by
eating ethyl gallate with pyroracemic acid and sulphuric
cid and proposed the so-called ketone-tannin formula :
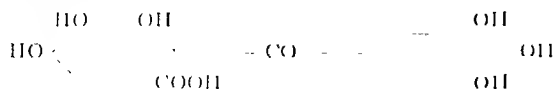
chiff completed this formula by a diagonal, so as to explain
e optical activity observed —
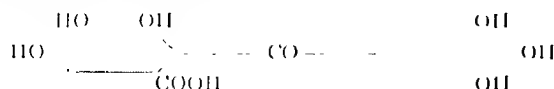
[1] *Ber.*, 1871, 4, 231.
[2] *Gazz chim. Ital.*, 1909, 39, 268.
[3] *Ber.*, 1898, 31, 3168.
[4] *Ibid.*, 1884, 17, 1476.

The ketone formula was corroborated by Nierenstein,[1] who distilled tannin with zinc dust and obtained diphenylmethane (smell of benzene) and a crystalline product, M.P. 70°-71° C. (M.P. of diphenyl = 71° C.). König and Kostanecki[2] sought to find the constitution of the tannins in the leuco-compounds of the oxyketones, to which catechin belongs. Nierenstein (see above), however, emphasises that the high molecular weight and the optical activity speak against the digallic acid formula, but in favour of this are the following points: (1) the decomposition of tannin with the formation of gallic acid; (2) the decomposition of methylotannin with the formation of di- and trimethyl esters of gallic acid; and (3) the production of diphenylmethane on distillation with zinc dust. The latter reaction especially illustrates the analogous formation of fluorene from compounds of the type—
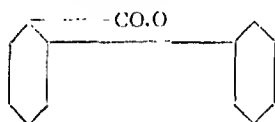
Nierenstein gave the name "Tannophor" to the mother-substance of tannin, phenylbenzoate, C_6H_5-COO-C_6H_5.

Dekker[3] was, however, unable to detect diphenylmethane on distilling with zinc dust, and did, therefore, not accept Nierenstein's views. In proposing the formula—
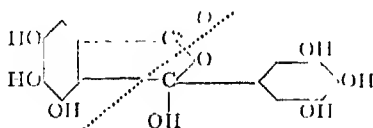
Dekker[4] was enabled to account for most of the details in the behaviour of tannin, viz.: (1) the empirical constitution, $C_{14}H_{10}O_9$; (2) the almost complete hydrolysis into gallic acid (the dotted line indicates the decomposition of the molecule into 2 molecules gallic acid by taking up water); (3) the

[1] *Ber.*, 1905, 38, 3641.
[2] *Ibid.*, 1906, 39, 4027.
[3] "De Looistoffen," vol. ii., p. 30 (1908).
[4] *Ber.*, 1906, 34, 2497.

ormation of diphenylmethane as a result of distillation with inc dust; and (4) the electrical non-conductivity. Since annin on acetylating yields a considerable amount of riacetylgallic acid, it should, according to Dekker, contain t least six acetylisable hydroxyls.

Nierenstein[1] objected to this formula on account of its containing seven hydroxyl groups, whereas Dekker found ix, Nierenstein five, and Herzig still fewer hydroxyl groups. The formula would also favour the conception of tinctorial properties which could hardly be ascribed to tannin. Lloyd[2] proposed a very intricate formula containing three digallic acid groups joined into one six-ring system, which would hen explain the optical activity; it would, on the other hand, lso require an inactive cis-form.

Iljin[3] prepared two phenylhydrazine derivatives of tannin $C_{74}H_{58}N_6O_{30}$ and $C_{98}H_{82}N_{14}O_{26}$) and proposed the formula, $C_{76}H_{40}O_{38}$, the constitution of which would be—

'here

$$R_1 = -CO.C_6H_2(OH)_3$$

nd

$$R_2 = -C_6H_2(OH)_3$$
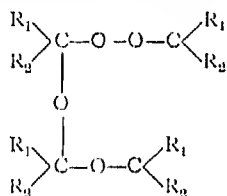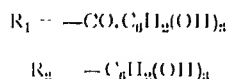
Nierenstein[4] considers tannin to be a mixture of digallic acid and leucotannin, the latter possessing the formula—
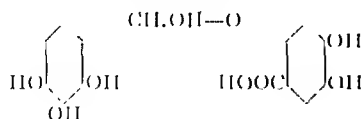
The optical activity of tannin is expressed in this formula

[1] *Chem. Ztg.*, 1906, 31, 880.

[2] *Chemical News*, 1908, 97, 133.

[3] *Jour. of the Russian phys. chem. Soc.*, 1908, 39, 470.

[4] *Ber.*, 1905, 38, 3841 ; 1907, 40, 917 ; 1908, 41, 77 and 3015 ; 1909, 42, 22 and 3552 ; *Chem. Ztg.*, 1907, 31, 72 ; 1909, 34, 15.

and its probability is corroborated by Nierenstein, who was able to resolve the acetylated tannin by fractional precipitation into pentacetyl tannin (M.P. 203°-208° C.) and pentacetyl leucotannin (M.P. 166° C.). By oxidation, the former is converted into ellagic acid, and on hydrolysis with dilute sulphuric acid readily yielded gallic acid. Hydrolysis of the pentacetyl leucotannin, however, yielded gallic aldehyde, and oxidation yielded purpurotannin (a naphthalene derivative) in addition to ellagic acid.

Nierenstein[1] also succeeded in converting tannin into carboethoxytannin, the latter on saponification yielding crystalline, inactive digallic acid. On acetylating pentacetyl leucotannin with acetyl chloride a hexacetyl derivative (M.P. 159° C.) is obtained, the strychnine salt of which is resolved into both of the active components. This proves the presence of digallic acid and leucotannin in tannin lev. pur. Schering investigated by Nierenstein. The latter author[2] later considered tannin to be polydigalloylleucodigallic acid anhydride and the simplest tannin to be a digalloylleucodigallic acid anhydride. This view, however, would not stand subsequent criticisms, being in disagreement with the earlier observations of molecular weight and acidic properties of tannin. Manning[3] believed to have isolated a pentethylester of the pentagalloyl glucoside from tannin, but this was shown to be the ethyl ester of gallic acid.

Feist[4] had arrived at the conclusion that tannin was a glucose compound, and maintained that tannin from Turkish galls was a compound of glucogallic acid combined as an ester with 2 molecules gallic acid. But Fischer and Strauss[5] synthetically prepared a glucoside of gallic acid exhibiting differences from Feist's preparation which were so great that the latter no longer could be considered a single glucoside of gallic acid.

Fischer and Freudenberg[6] subsequently elaborated a

[1] *Ber.*, 1910, 43, 628.
[2] Liebig's *Ann.*, 1912, 386, 318 ; 388, 223.
[3] *Ibid.*, 1912, 34, 918.
[4] *Ber.*, 1912, 45, 1493.
[5] *Ibid.*, 1912, 45, 3773.
[6] *Ibid.*, 1912, 45, 2717 ; 1913, 46, 1127.

iethod of purifying tannin, and on investigating the purified
ibstance, arrived at the conclusion that no other hydroxy-
enzoic acid than gallic acid was present in tannin.   On
:peating Strecker's hydrolysis they obtained 7-8 per cent.
igar, and hence concluded that 1 molecule of glucose was
)mbined with about 10 molecules of gallic acid.   Owing to
ie difficulty of isolating the intermediary hydrolysis products,
id the subsequent impossibility of drawing any conclusions
; to the constitution of tannin, the latter investigators
:cided to adopt the methods offered by synthesis.   Their
isic idea was the absence of carboxylic groups in tannin,
id that hence the total gallic acid must be present in ester
rm.   These conditions are fulfilled if one views tannin as
:ing an ester compound of 1 molecule of glucose and
molecules of digallic acid, of similar construction as, for
:ample, pentacetyl glucose.   Fischer and Freudenberg
:cceeded in preparing the former by shaking a mixture of
iely powdered glucose, chloroform, and quinoline with an
:cess of tricarbomethoxygalloyl chloride for twenty-four
)urs and precipitating the resulting product with methyl
cohol ; suitably purified, a light amorphous colourless
bstance was obtained which proved to be penta- (tri-
rbomethoxygalloyl) glucose.   Careful saponification with
:cess alkali in acetone-aqueous solution at room temperature
elded a tannin very closely resembling tannin, identified as
ntagalloyl glucose.   It is doubtful, however, whether this
bstance is homogeneous, and it is probably a mixture of
'o stereoisomers.

Fischer and Freudenberg, therefore, further concluded
at tannin is mainly an ester compound of glucose and
nolecules *m*-digallic acid.   Elucidation on this point offered
elf advantageously in Herzwig's methylotannin,[1] which is
tained by the interaction of diazomethane and tannin.
ie first step was then to prepare pentamethyl-*m*-digallic acid

$$CH_3.O \overset{O.CH_3}{\underset{O.CH_3}{\Big<}} \Big>\!\!-\!\!-\!\!-CO.O-\!\!-\!\!-\Big< \overset{COOH}{\underset{CH_3.O \quad O.CH_3}{}}$$
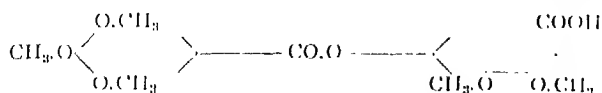
[1] *Ber.*, 1905, 38, 989.

from trimethylgalloyl chloride and the *m-p*-dimethyl ether of gallic acid; the chloride of this substance, coupled with α- and β-glucose, yields—
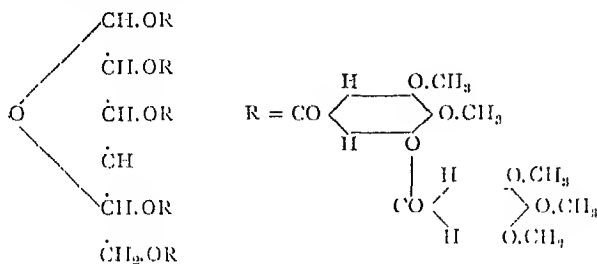
Penta- (pentamethyl-*m*-digalloyl) -glucose.

The α- and β-derivatives thus obtained differ in their behaviour towards polarised light, and are, again, probably mixtures of two stereoisomers, *i.e.*, mixtures of derivatives of α- and β-glucose. Compared to methylotannin, these preparations exhibit very close resemblance to the former, from which it may be concluded that they are closely related to this substance, and probably possess the same or a very similar structure; the result of the above experiments has, therefore, brought us at least in close proximity to the structure of tannin. It must, however, be borne in mind that the analysis and hydrolysis of tannin does not afford an explanation of the question as to whether tannin is a compound of glucose and 10, 9, or 11 molecules of gallic acid; it is also possible, though not probable, that tannin would contain a polysaccharide instead of glucose itself. Similarly to sugar, the true glucosides can be coupled with hydroxy-benzoic acids, which is proved by the preparation of tetra-galloyl-α-methyl glucoside; this substance, also, exhibits tannoid character.

2. Digallic Acid

Whereas, until recently, tannin had been considered to be gallic acid anhydride, or digallic acid, closer investigations have revealed that neither is tannin digallic acid nor is the synthetically prepared digallic acid identical with tannin.

Schiff[1] prepared digallic acid by the interaction of phosorus oxychloride and gallic acid, and believed the product :ained to be identical with tannin ; to this latter he first :ribed an ether formula (I.), later an ester formula (II.) ··

$$C_6H_2 <^{(OH)_2}_{COOH} --- O --- ^{(OH)_2}_{HOOC}> C_6H_2 \qquad C_6H_2(OH)_3 -C- .O.C_6H_2 <^{(OH)_2}_{COOH}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \underset{O}{\|}$$

(I.)   (II.)
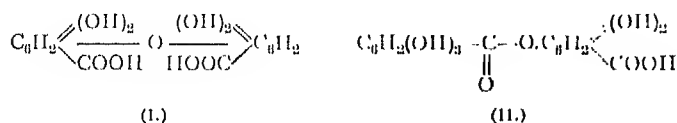
Froda[2] held that Schiff's condensation product contained osphorus or arsenic acid and ascribed its tanning properties the latter ; according to this investigator, digallic acid, en completely freed from arsenic acid, does not react with atine or quinine. Biginelli[3] did not consider the action arsenic acid that of a catalyst, but held that it entered o.reaction ; according to his investigations products conning arsenic ($C_7H_7O_8As$ and $C_{14}H_{11}O_{12}As$) are obtained en gallic acid is heated with arsenic acid.

In his preparation of digallic acid, Iljin[4] could only obtain lic acid, and the ethyl ether of gallic acid showing no iracteristics of the tannins ; when, however, he heated gallic d with arsenic pentoxide, he obtained bodies exhibiting : reactions given by tannins.

Böttinger[5] made the first attempt at synthesising tannin ; heated gallic acid or its ethyl ester with glyoxylic acid or ·oracemic acid, and obtained a substance of the composi1 $C_{14}H_{10}O_9.2H_2O$, which certainly showed some of the iracteristics exhibited by tannin, but which by no means s identical with the latter. Böttinger's preparation is obably identical with β-digallic acid, one of two dibasic mers having the composition—

$$C_6H_2(OH)_3COOH$$
$$|$$
$$C_6H(OH)_3COOH$$
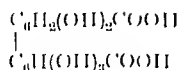
[1] *Ber.*, 1871, 231 and 967.
[2] *Ga : z. chim.*, 1878, 9.
[3] *Ibid.*, 1909, 39, ii. 268 and 283.
[4] *Jour. f. prakt. Chem.*, 1911, 82, 451.
[5] *Ber.*, 1884, 1503.

the other possible isomer having the composition

$$CO{<}\begin{matrix} C_6H(OH)_3COOH \\ C_6H_2(OH)_3 \end{matrix}$$
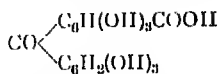
Fischer[1] obtained a digallic acid (M.P. 275°-280° C.) by coupling tricarbomethoxygalloyl chloride with dicarbomethoxygallic acid.

Nierenstein[2] obtained, from the carbethoxy compound of tannin, a crystalline, optically active digallic acid, M.P. 268°-270° C. The pentacetate of this substance, obtained by reduction and acetylisation, yielded hexacetylleucotannin. A pentamethyldigallic acid methyl ester of the composition

$$(O.CH_3)_3C_6H_2{\longrightarrow}COO{\longrightarrow}C_6H_2(OCH_3)_3COO.CH_3$$
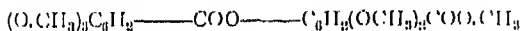
was obtained by Mauthner[3] from the chloride of trimethylgallic acid and the methyl ester of the acid from the glucoside of syringin; on saponification with caustic potash the former compound yielded trimethylgallic acid and syringic acid. Fischer[4] synthesised the so-called *m*-digallic acid by coupling tricarbomethoxygalloyl chloride with carbonylgallic acid and subsequent splitting off of CO_2. The *m*-digallic acid appears as rather thick, colourless, microscopic needles containing about 16 per cent. water of crystallisation, M.P. 271° C. They are slightly soluble in cold, soluble in hot water, and very soluble in methyl and ethyl alcohols. Their aqueous solution gives dark blue coloration with ferric chloride, and precipitates gelatine and quinine.

Fischer and his students[5] prepared quite a number of digallic acid derivatives, amongst which are the following :

Pentamethyl-*m*-digallic acid methyl ester, $C_{20}H_{22}O_9$.
Pentacetyl-*m*-digallic acid, $C_{24}H_{20}O_{11}$.
Pentamethyl-*m*-digallic acid, $C_{19}H_{20}O_9$.
Pentamethyl-*m*-digalloyl chloride, $C_{19}H_{19}O_8Cl$.
Pentamethyl-*p*-digallic acid, $C_{19}H_{20}O_9$.
Pentamethyl-*p*-digallic acid methyl ester, $C_{20}H_{22}O_9$.

[1] *Ber.*, 1908, 41, 2875.
[2] *Ibid.*, 1910, 43, 628.
[3] *Jour. f. prakt. Chem.*, 1911, 84, 140.
[4] *Ber.*, 1913, 46, 1116.
[5] *Ibid.*, 1912, 45, 915, 2707 ; 1913, 46, 1116.

Hydrolysis of digallic acid yields gallic acid ; oxidation,
the other hand, ellagic acid and luteic acid (Luteo Säure),
ich can be separated by shaking with pyridine. The
uction of digallic acid yields, by different methods, the
ie reduction compound,[1] viz., the racemic leucodigallic acid,
ich differs from digallic acid by being devoid of any
noid properties; the latter distinction may be ascribed
the transformation of the tannophor group —CO.O—, to
tannoid-inactive group CH(OH)—O—.

The successful resolving of racemic leucodigallic acid into
h of its optically active components can only be brought
ut through the d- or l-hexacarbethoxyleucodigallic acid
introducing the latter into a 1 per cent. pyridine solution
l heating to 45°-50° C., whereby the d- or l-acid is formed
companied by a strong evolution of carbon dioxide.

Hydrolysis of leucogallic acid yields gallic acid and gallic
ehyde ; oxidation by means of hydrogen peroxide yields
gic acid and luteic acid, and oxidation with potassium
sulphate and sulphuric acid, in acetic acid solution, yields
purotannin (see below).[2]

Another distinct difference between digallic acid and
codigallic acid is the fact that the formaldehyde conden-
on product of the former resembles gallic acid, whereas
t of the latter resembles tannin ; it is therefore probable
t the leucodigallic acid part of the tannin molecule imparts
characteristic property to tannin.

Digallic Acid.

Lutere Acid.

Ellagic Acid.

Purpuro Tannin.

Nierenstein, Abderhalden's "Handb. d. biochem. Arbeitsm.," vi. 154.
Liebig's *Ann.*, 1912, 386, 318.
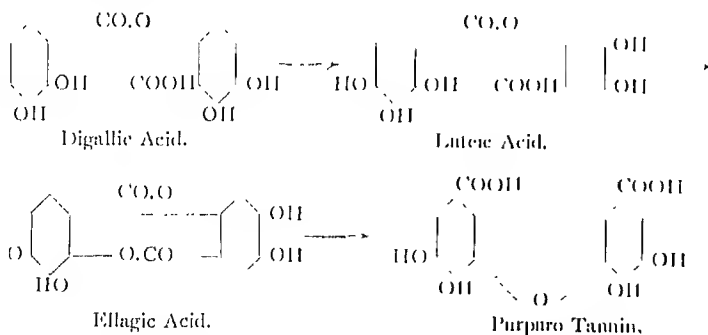
3. Ellagic Acid

Ellagic acid was discovered in 1831 by Braconnot, who named it "acide ellagique." Its presence in the vegetable kingdom was not quite comprehended for some time, and Nierenstein[1] was the first to prepare this substance from algarobilla, dividivi, oak bark, pomegranate, myrabolams, and valonea. The acid is obtained by precipitating it with water from a hot alcoholic extraction of the plants referred to, and recrystallising the precipitate from hot alcohol. Another method of preparation consists in boiling the disintegrated plants with dilute hydrochloric acid, washing the residue, and extracting with hot alcohol, from which the acid will then crystallise. According to Löwe,[2] it may be obtained from dividivi, an aqueous extract of which is heated to 110° C. in a tube closed at both ends, when crystalline ellagic acid is deposited. Heinemann[3] obtained ellagic acid by simply boiling repeatedly aqueous tannin solutions.

Löwe[4] first synthesised ellagic acid by heating gallic acid with arsenic acid or silver oxide. Herzig[5] states that ellagic acid is deposited when air is conducted through a mixture of the ethyl or methyl ester of gallic acid and ammonia. Perkin[6] obtained a substance very similar to ellagic acid by electrolysis of gallic acid in sulphuric acid solution ; on oxidising gallic acid in concentrated sulphuric acid solution, Perkin and Nierenstein[7] obtained flavellagic acid. Ellagic acid is also obtained by heating luteic acid in a 10 per cent. soda solution.

Ellagic acid thus prepared crystallises with 2 molecules of water as yellow micro-crystalline rhombic prisms or prismatic needles. The crystals lose this water when heated to 100° C., and it is possible that it is water of constitution, in which case the substance would be hexoxydiphenylcarboxylic acid, and

[1] *Chem. Ztg.*, 1909, 87.
[2] *Zeits. f. analyt. Chem.*, 1875, 35.
[3] Ger. Pat., 137,033 and 137,934.
[4] *Jour. f. prakt. Chem.*, 1868, 103, 464.
[5] *Monatshefte für Chemie*, 1908, 29, 263.
[6] *Proc. Chem. Soc.*, 1905, 21, 212.
[7] *Ibid.*, 1905, 21, 185.

substance left after drying at 100° C., the dilactone.[1]
agic acid is slightly soluble in water, alcohol, and ether, but
easily soluble in caustic potash. With concentrated nitric
the product assumes a red colour, which appears to be
to the presence of impurities; ellagic acid is commercially
own as "alizarin yellow."

The constitution of ellagic acid was uncertain for a long
e, and different structural formulæ were proposed which
re or less corresponded to its properties. The most satis-
tory structural formula was proposed by Graebe—[2]
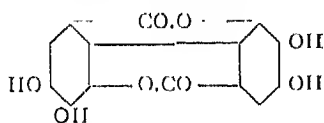
is would represent a tetroxydiphenylmethylolide.

The probability of the correctness of this formula is sup-
ted by the possibility of the following derivatives: mono-
thylellagic acid, $C_{14}H_5O_7(O.CH_3)$; dimethylellagic acid,
$H_4O_6(O.CH_3)_2$; tetramethylellagic acid, $C_{14}H_2O_4(O.CH_3)_4$;
enylhydrazinellagic acid, $C_{14}H_6O_8.N_2H_3C_6H_5$.

By the electrolytic reduction of ellagic acid, hexoxy-
phenyl, $(OH)_3C_6H_2 — C_6H_2(OH)_3$, is obtained; the ordinary
thods of reduction yield leucoellagic acid, $C_{14}H_{10}O_8$, which
stallises in small sharp needles, melting with decomposition
294°-295° C. Leucoellagic acid is soluble in ethyl and methyl
ohols, and in glacial acetic acid, insoluble in chloroform,
zene, toluene, carbon tetrachloride, and petrol ether; it
es a bluish-green colour with ferric chloride which quickly
ns black. Leucoellagic acid is soluble in alkalies, the
ution assuming a deep-red coloration; it reduces silver
rate in the cold, but is not adsorbed by mordanted cotton
th, in which respect it differs from ellagic acid.[3]

Ellagitannic Acid, $C_{26}H_{28}O_{10}.3H_2O$, is closely related to
agic acid; the former consists of faintly yellow needles,
P. 329°-336° C. It is soluble in water, precipitates gelatine,

[1] *Arch. d. Pharm.*, 1907, 244, 575.

[2] *Chem. Ztg.*, 1903, 129.

[3] Liebig's *Ann.*, 1912, 394, 249.

and is adsorbed by hide powder. It occurs with gallic acid, tannin, and ellagic acid in dividivi, myrabolams, algarobilla, and chestnut wood extracts.

Other bodies of this class include :—

Metellagic Acid, $C_{14}H_8O_6$, derived from methoxybenzoic acid, and recrystallised from acetic acid, forms small crystalline needles, M.P. 273°-276° C., and yields fluorene on distillation with zinc dust.

$$\text{CO.O}$$
$$\text{O.CO} \qquad \text{OH}$$
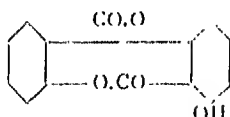
Flavellagic Acid, $C_{14}H_6O_9$, is obtained by the oxidation of gallic acid with concentrated sulphuric acid and potassium persulphate. It crystallises from pyridine in prismatic needles melting above 360° C. Distillation with zinc dust yields fluorene (see above)—

$$\text{HO} \quad \text{CO.O} \quad \text{OH}$$
$$\text{OH} \quad \text{O.CO} \quad \text{OH}$$
$$\text{OH} \qquad \text{OH}$$
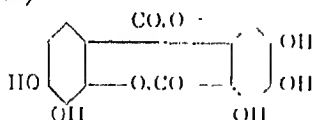
By heating ellagic acid for three-quarters of an hour at 185° C. with concentrated sulphuric acid, ceruleo-ellagic acid (dioxyellagic acid), $C_{14}H_8O_{10}$, is formed as yellowish needles, M.P. 360° C., which are but little soluble in the usual solvents. The acid is slightly soluble in strong caustic soda solution, the colour of the solution, on diluting, changing to green and blue.

Luteic Acid (Luteo Säure, pentoxybiphenylmethylolide carboxylic acid), $C_{14}H_8O_9$, occurs, in addition to ellagic acid, in myrabolams—[1]

$$\text{CO.O}$$
$$\text{HO} \quad \text{OH} \qquad \text{OH}$$
$$\text{HOOC} \quad \text{OH}$$
$$\text{OH}$$
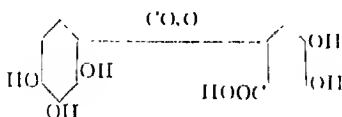
It is obtained by extracting myrabolams for one hour and a half, under reflux condenser, with pyridine, filtering

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[1] *Ber.*, 1909, 42, 353.

l adding twice the volume of water to the filtrate and ling till complete solution is obtained. After about thirty rs a reddish powder deposits, from which ellagic acid y be extracted with pyridine; the mother-liquor on being centrated yields luteic acid. It is also obtained by dising tannin with hydrogen peroxide, the other oxidation duct being ellagic acid, and the two may then be separated indicated above. Luteic acid forms reddish needles which decomposed, with evolution of gas, at 338°-341° C. ated with 10 per cent. caustic soda solution it yields ellagic d. In pyridine solution the carboxyl group may be eliminated hydrogen iodide, whereby pentoxybiphenylmethylolide formed as long silky needles, which do not melt below ɔ° C. The same substance may also be obtained when gic acid is boiled with concentrated caustic potash solution. hen luteic acid is treated with diazomethane, it yields the thyl ester of pentamethoxybiphenylmethylolidecarboxylic d.

4. Depsides

The most common decomposition products of the natural moids are hydroxybenzoic acids, notably gallic and proto-techuic acids; furthermore, other aromatic and aliphatic droxy compounds frequently occur. So far, however, empts at explaining the constitution of the complex composition products obtained by hydrolysing high lecular tannoids have not been successful. On the other nd, the constitution of the simpler natural tannoids is own to a greater or less extent; of these, lecanoric acid ecanorsäure) is the best known, being an ester anhydride orsellic acid (a dihydroxytoluylic acid). It combines with ythrite, forming another tannoid, erythrine. The fact that droxybenzoic acids are constantly encountered together th the products obtained on hydrolysis of the tannins, seems point toward the conclusion that anhydrides of hydroxy-nzoic acids are frequent constituents of the natural tannoid lecules.

The assumption that, for instance, in tannin at least part the gallic acid radicals are combined with one another is

highly probable, and is supported by the formation of tri- and dimethylgallic acid from methylotannin,[1] and by the formation of ellagic acid when tannin is oxidised.[2] Further proof is brought forward by the existence of the pentacetyl-tannin,[3] and by the results of hydrolysis which has yielded up to 104 per cent. anhydrous gallic acid from tannin.[4]

Of the three classes of isomeric anhydrides which can be formed from hydroxybenzoic acids, the chemistry of the natural tannins is only concerned with the class comprising the ester anhydrides. If the carboxyl of the first molecule combines with a hydroxyl of the second molecule (ester formation), then a substance possessing character similar to that of a hydroxybenzoic acid is formed, which is capable of combining up with a further molecule in the same way. It is natural to assume that this ester form is much more prevalent in Nature than a combination of two carboxyls by the elimination of water. From the point of view of the chemistry of the tannins, therefore, the starting-point would naturally be that of synthesising the ester anhydrides of hydroxybenzoic acids. Amongst the small number of synthetically prepared ester anhydrides of hydroxybenzoic acids, a few occur exhibiting the properties of the natural tannoids.

In order to simplify the terminology of these substances, Fischer[5] proposed the name " Depsides " from δεψειν = to tan. In analogy with peptides and saccharides, the names di-, tri-, and polydepsides of hydroxybenzoic acids would be suitable for these substances.

The principles underlying the synthesis of depsides are the following :—If the chlorides of carbomethoxy (or carbeth-oxy) hydroxybenzoic acids are coupled with the sodium salts of hydroxybenzoic acids, esters are formed, e.g.,

$$CH_3CO.O.O.C_6H_4.CO.Cl + NaO.C_6H_4.COO.Na = NaCl$$
$$+ CH_3.COO.O.C_6H_4.CO.O.C_6H_4.COO.Na$$
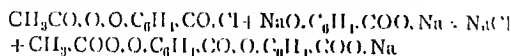
[1] Herzig, *Monatshefte f. Chemie*, 1909, 30, 543.
[2] Nierenstein, *Ber.*, 1908, 41, 3015.
[3] Schiff, *Ann. d. Chem.*, 1873, 170, 73.
[4] Sisley, *Bull. Soc. Chim.*, 1909, 5, 727.
[5] Liebig's *Ann.*, 1910, 372, 35.

gently saponifying the esters, these are converted into corresponding hydroxy derivatives—

$$OH.C_6H_4.CO.O.C_6H_4.COOH$$
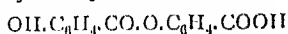
According to Fischer and Freudenberg,[1] this method sesses the following advantages :—

1. The synthesis takes place at low temperatures, so that intramolecular rearrangements are improbable.

2. The composition of the substances is controlled by intermediary compounds, the carboalkyloxy deriva- s.

3. The synthesis permits of more definite evidence as rds the structure of the resulting compounds.

4. The substances obtained are easily purified.

Depsides produced in this manner are by no means new, were obtained by Klepl by simply heating p-hydroxy- zoic acid (cf. Introduction, p. 4). This simple procedure, ever, is not applicable to most other hydroxybenzoic s which are decomposed at the high temperature neces- to induce reaction. Löwe and Schiff (loc. cit.) have ained products similar to tannins, the latter investigator removing the elements of water from gallic acid, proto- chuic acid, salicylic acid, m-hydroxybenzoic acid, cresotinic , phloretinic acid, and pyrogallolcarboxylic acid. These sides, however, are amorphous substances, and it is hence cult to substantiate their homogeneity.

Carbomethoxylation of Hydroxybenzoic Acids

Amongst other compounds chlorohydroxybenzoic acid sed in the preparation of the materials employed in the hesis of depsides ; the free phenolic group, however, ·ts a disturbing influence when aromatic acids are acted n by phosphorus chloride, and another group, which can sequently be easily removed, must therefore be introduced cover the disturbing influence referred to. For this oose, Fischer[2] chose the carbomethoxy group, and this stigator succeeded, by the action of chlorocarbonic alkyl

[1] Liebig's *Ann.*, 1909, 372, 32.
[2] *Ber.*, 1908, 41, 2860.

ester and alkali upon hydroxybenzoic acid in cold aqueous solution, in obtaining substances with the properties required.[1] In such substances (*e.g.*, salicylic acid) where the hydroxyl occupies the ortho-position to the carboxyl, complete carbomethoxylation does not take place, whereas the *m*- or *p*-positions offer no hindrance. In the case of the *o*-position, however, the action of chlorocarbonic alkyl ester is successfully assisted by the presence of dimethylaniline in an inert solvent, *e.g.*, benzene.[2] The difficulty encountered by the *o*-position is eliminated when the carboxyl is not directly linked to the benzene nucleus, *e.g.*, *o*-cumaric acid. Many hydroxybenzoic acids require an excess of chlorocarbonic methyl ester, which then also, to some extent, attacks the carboxyl group; but on dissolving the product in acetone and treating it with bicarbonate the carboxyl group as such is again restored without splitting off the carbomethoxy group.[3] In this way all hydroxybenzoic acids may be carbomethoxylated.[4] The carbomethoxy group is easily removed by excess of aqueous alkali in the cold, and is also partially removed when insufficient alkali is present; the latter fact is of importance in the synthesis of didepsides.

Chlorides of Carbomethoxyhydroxybenzoic Acids

The chlorides of these compounds are obtained when phosphorus pentachloride is allowed to act upon the acids, and are as a rule crystalline. For the purpose of synthesis they may be employed as follows :—

1. They readily form esters with alcohols, which on subsequent saponification with alkali are converted into the esters of the free hydroxybenzoic acids.

2. The chlorides interact energetically with esters of amino-acids, and may be coupled with amino-acids in aqueous alkaline solution. On subsequently removing the carbo-

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[1] *Ber.*, 1908, 41, 2875.

[2] U.S. Pat., 1,639,174, 12, xii., 1ꞌ 99.

[3] *Ber.*, 1913, 46, 2400.

[4] *Ibid.*, 1908, 41, 2877, 2881, 2882 ; 1909, 42, 226, 218, 223, 225 ; Liebig's *Ann.*, 1912, 391, 357, 366 ; *Ber.*, 1913, 46, 1145, 2390, 2400.

oxy group derivatives of hydroxybenzoic acids are
...ned, *e.g.*,

$$CH_3.CO_2.O.C_6H_4.CO.Cl + 2NH_2CH_2.CO.C_2H_5$$
$$...NH_2.CH_2.CO_2.C_2H_5 + HCl + CH_3.CO_2.O.C_6H_4.CO.NH.CH_2CO_2C_2H_5.$$
$$CH_3.CO_2.O.C_6H_4.CO.NH.CH_2.CO_2.C_2H_5 + 3NaOH$$
$$= Na_2CO_3 + C_2H_5OH + CH_3OH + HO.C_6H_4.CO.NH.CH_2.COONa.$$
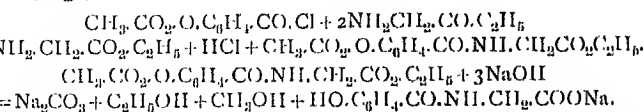
In the presence of $AlCl_3$ the chlorides easily combine
...benzene, and on removing the carbomethoxy group
...nmetrical hydroxy derivatives of benzophenone are
...d :—

$$...CH_3.CO_2.O.C_6H_4.CO.Cl + C_6H_6 = CH_3.CO_2.O.C_6H_4.CO.C_6H_5 + HCl$$
$$CH_3.CO_2.O.C_6H_4.CO.C_6H_5 + 3NaOH$$
$$= NaO.C_6H_4.CO.C_6H_5 + Na_2CO_3 + CH_3OH + H_2O.$$
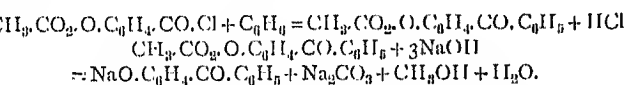
The chlorides may be coupled with free hydroxybenzoic
...and on removing the carbomethoxy group didepsides
...btained. Repetition of these operations yields tri- and
...lepsides.

Preparation of Didepsides

...simple application of these syntheses is offered by
...roxybenzoic acid. When the chloride of its carbo-
...oxy derivative is allowed to interact with *p*-hydroxy-
...ic acid in aqueous alkaline solution, in the cold, the
...salt of carbomethoxy - *p* - hydroxybenzoic acid is
...ed : — [1]

$$CH_3.CO_2.O.C_6H_4.CO.Cl + NaO.C_6H_4.COONa$$
$$CH_3.CO_2.O.C_6H_4.CO_2.C_6H_4.CO_2.Na + NaCl.$$
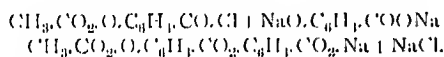
...eing sparingly soluble, the salt in this case is readily
...sited as crystals, but is readily converted into the free
...by hydrochloric acid. In most other cases, however,
...lkali salts are easily soluble and the aqueous solution
...n directly acidified with a mineral acid. The chlorides,
...for the most part solids, the mode of procedure is as
...ws :—the hydroxybenzoic acid required for coupling is
...lved in normal or double-normal alkali (the volume
...lated per molecule acid), a little acetone added, and the
...ure well cooled ; a further molecule of 2N caustic soda
...the chloride (1 molecule) dissolved in dry acetone are

[1] *Ber.*, 1909, 42, 216.

added in small portions, whilst stirring, to the mixture. In spite of the low temperature the coupling proceeds quickly and the sparingly soluble product can in most cases be precipitated from the solution by acidifying and diluting with water. In case of more easily soluble coupling products the acetone is driven off under reduced pressure or the liquid acidified and diluted, and the substance extracted with ether. Instead of alkali, dimethylaniline may be employed, with the exclusion of water as a solvent for the purpose of coupling.

Another suitable method of obtaining o-didepsides is that of treating o-hydroxybenzoic acids with phosphorus trichloride and dimethylaniline (e.g., synthesis of disalicylic acid, Boehringer & Sons).[1]

The carbomethoxy derivatives of the depsides are as a rule crystalline substances of distinct acidic character, and decompose alkaline carbonates.

The elimination of the carbomethoxy group may be brought about by dilute alkaline solutions in the cold, or by aqueous ammonia. If the depside formed is so stable as to resist the action of alkali for several hours, the use of the latter is very convenient for the purpose required. The substance is dissolved directly in sufficient normal alkali to neutralise the carboxyl group and a further 2 molecules of caustic soda for each carbomethoxy group to be eliminated are added. The temperature should be about 20° C., when the reaction as a rule is completed after one-half to three-quarters of an hour. It is usual, however, to use an aqueous ammonia solution in considerable excess, whereby the temperature should again be about 20° C., and the solution of ammonia normal or half normal.

The didepsides so far investigated are crystalline bodies, sparingly soluble in cold water ; they—as a rule—decompose when fused, possess acid reaction, and are dissolved by bicarbonates. On account of the presence of a free phenolic group they give a coloration with ferric chloride ; if the phenolic group occupies the o-position to carboxyl, the coloration with ferric chloride is red or bluish-violet. Excess of dilute alkali resolved all didepsides into their components

[1] Ger. Pat., 211,403.

inary temperatures. The didepsides of gallic, proto-
uic, gentisinic, and β-resorcylic acids precipitate gelatine
iinine acetate, and in this respect approach the natural
is.

ic following summary gives an account of depsides
have been prepared synthetically or which occur
 illy :— [1]

> Di-*p*-hydroxybenzoic acid.
> Di-*m*-hydroxybenzoic acid.
> Disalicylic acid.
> Diprotocatechuic acid.
> Digentisinic acid.
> Di-β-resorcylic acid.
> *p*-Diorsellic-acid.
> *o*-Diorsellic acid.
> *m*-Digallic acid.
> Disyringic acid.
> Di-*o*-cumaric acid.
> Diferulic acid.
> Di-β-hydroxynaphthoic acid.
> *p*-Hydroxybenzoyl-*m*-hydroxybenzoic acid.
> *m*-Hydroxybenzoyl-*p*-hydroxybenzoic acid.
> Salicyl-*p*-hydroxybenzoic acid.
> Vanilloyl-*p*-hydroxybenzoic acid.
> Feruloyl-*p*-hydroxybenzoic acid.
> α-Hydroxynaphthoyl-*p*-hydroxybenzoic acid.
> Orsellinoyl-*p*-hydroxybenzoic acid.
> Protocatechuyl-*p*-hydroxybenzoic acid.
> Galloyl-*p*-hydroxybenzoic acid.
> Pyrogallolcarboyl *p*-hydroxybenzoic acid.
> Syringoyl-*p*-hydroxybenzoic acid.
> *p*-Hydroxybenzoyl-syringic acid.
> Pentamethyl-*m*-digallic acid.
> Pentamethyl-*p*-digallic acid.
> Vanilloyl vanillin.

Preparation of Tridepsides

Ionohydroxybenzoic acids allow theoretically of tri-

Ber., 1908, 41, 2888 ; 1909, 42, 217 ; 1912, 45, 2718 ; 1913, 46, 1130, 1141, 1143 ; Liebig's *Ann.*, 384, 230, 233, 238 ; 391, 356, 362.

depsides of the type $HO.C_6H_4COO.C_6H_4.COO.C_6H_4.COOH$ only; if, on the other hand, di- or trihydroxybenzoic acids are dealt with, two formulæ are possible, viz. :—

$$\left.\begin{array}{l} HO.C_6H_4.COO \\ HO.C_6H_4.COO \end{array}\right\rangle C_6H_3.COOH$$
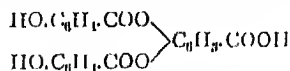
Of the former type, two compounds are known, *i.e.*, di-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid and vanilloyl-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid —

$$\left.\begin{array}{l} HO \\ CH_3O \end{array}\right\rangle C_6H_3.COO.C_6H_4.COO.C_6H_4.COOH$$
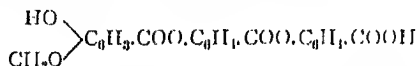
The first named of these two compounds was obtained by Klepl, in addition to the didepside, by heating *p*-hydroxybenzoic acid. Fischer and Freudenberg obtained a beautifully crystalline form in the following way : carbethoxyhydroxybenzoyl chloride was coupled with *p*-hydroxybenzoyl-*p*-hydroxybenzoic acid in alkaline solution, the compound dissolved in a mixture of pyridine and acetone, and ammonia added for the purpose of removing the carbethoxy group. The tridepside was then obtained as long needles by redissolving in acetone.

Both tridepsides melt well above 200° C., are practically insoluble in water, and are but sparingly soluble in practically all organic solvents. In alcoholic solution they give colour reaction with ferric chloride similar to those given by *p*-hydroxybenzoic acids.

Preparation of Tetradepsides [1]

Here, again, two forms are known, *e.g.*, tri-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid —

$$HO.C_6H_4.COO.C_6H_4.COO.C_6H_4COO.C_6H_4.COOH$$
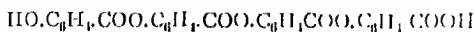
and vanilloyl-di-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid—

$$\left.\begin{array}{l} HO \\ CH_3O \end{array}\right\rangle C_6H_3.COO.C_6H_4.COO.C_6H_4.COO.C_6H_4.COOH$$
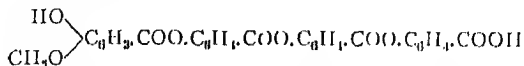
The former has been prepared from carbethoxyhydroxybenzoyl-*p*-hydroxybenzoyl chloride and *p*-hydroxybenzoyl-*p*-

---

[1] Fischer and Freudenberg, Liebig's *Ann.*, 1910, 372, 32.

hydroxybenzoic acid in alkaline solution; the second tetradepside was prepared from carbomethoxyvanilloyl-*p*-hydroxybenzoyl chloride and *p*-hydroxybenzoyl-*p*-hydroxy-benzoic acid.

The preparation of these compounds is rendered difficult by the slight solubility of the substances and their slight affinities for entering into reaction. Both tetradepsides were obtained in crystalline form, and are but very little soluble in most organic solvents. They decompose on being fused.

Tannoid Substances of the *Tannin* Type

The preparation of pentagalloyl glucose has proved this compound to be nearly identical with tannin obtained from galls (*tannin*); a few other natural tannins belong to this type which Fischer terms acyl compounds of sugar with hydroxybenzoic acids. The method of preparation employed in the synthesis of pentagalloyl glucose may be easily applied to other hydroxybenzoic acids, *e.g.*, penta[*p*-hydroxybenzoyl] glucose [1] was prepared in this way. Similar characteristics are exhibited by pentasalicylo glucose. Mention must also be made of the corresponding derivative of pyruvic acid and the compound with pyrogallolcarboxylic acid, penta-[pyrogallolcarboyl] glucose.[2] The latter is isomeric with pentagalloyl glucose and possesses similar properties; there is, however, a vast difference in the solubility of the two. Whereas the galloyl compound is easily soluble in cold water, its isomer is hardly soluble in hot, and completely insoluble in cold water. Considering the very similar structure of these two tannins, such differences appear surprising, but an analogy may be readily found in the existence of colloidal solutions of tannin and the (nearly) identical pentagalloyl glucose. These properties clearly show how dependent is the colloidal state on small differences in the structure of two substances. On the other hand, the formation of hydrosols is of the greatest importance relatively

[1] Fischer and Freudenberg, *Ber.*, 1912, 45, 933.

[2] Fischer and Rapoport, *Ber.*, 1913, 46, 2397.

to the part played by these substances in Nature as well as
relating to their chemical characteristics; thus it is extremely
difficult to make a solution of penta-[pyrogallolcarboyl]-
glucose, at the same time ascertaining its astringent taste
and its property of precipitating gelatine.

The experience gained by the methyl glucosides makes
it exceedingly probable that the simpler polyhydric alcohols
also are suitable substances to employ in these syntheses;
as a matter of fact, glycerol has been condensed with gallic
acid.[1]

One of the chief characteristics of synthetic tannins is
their high molecular weight; for instance, the molecular
weight of penta-[tricarbomethoxygalloyl]-glucose is 1,810,
that of penta-[pentamethyl-m-digalloyl]-glucose 2,051.
Employing gallic acid derivatives, especially the tribenzoyl
compounds, coupled with glucose, $e.g.$, mannite, yielded a
neutral ester of molecular weight 2,967.

The determination of the elementary composition of
compounds of high molecular weight is greatly facilitated
by employing their halogen derivatives; so, for instance,
is p-iodophenyl maltosazone very suitable. Coupling the
latter with tribenzoylgalloyl chloride yielded hepta-[tribenzoyl-
galloyl]-p-iodophenyl maltosazone, the structure of which is
represented by—

$$CH : N_2H.C_6H_4I$$
$$|$$
$$C : N_2H.C_6H_4I$$
$$|$$
$$CH.O.R \qquad\qquad R = CO.C_6H_2(O.CO.C_6H_5)_2$$
$$|$$
$$CH.O.R$$
$$|$$
$$CH.O.R \quad\ R\ R \qquad R\ R$$
$$|\qquad\quad O\ O \qquad\ O\ O$$
$$CH_2.O.CH.CH.CH.CH.CH.CH_2$$
$$\diagdown\quad\diagup$$
$$O$$
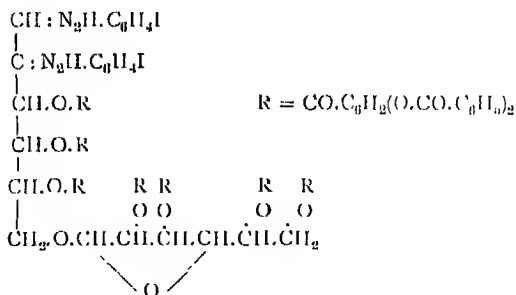
The molecular weight of this substance is 4,021, and
probably represents the highest molecular organic body
obtained in any chemical synthesis.

[1] Fischer and Freudenberg, *Ber.*, 1912, 45, 935.

From a physiological standpoint the recognition of tannins as esters of glucose and hydroxybenzoic acids, possessing characteristics similar to those of tannin, is of great importance. Especially interesting appears the fact of plants utilising sugars for the esterification of acids, just as glycerol or monohydric alcohols may be employed for the same purpose. Free acids, as a rule, are only tolerated in certain parts of the organism, the latter usually striving to neutralise acidic groups which may be brought about by salt formation; formation of amino compounds (proteins) or esterification (fats); and, lastly, esterformation by means of sugars.

Why Nature should always build up substances of very complex constitution can only be explained by biochemical investigations, but it may, at any rate, be assumed that by this means any substance poisonous to the living organism is rendered inactive. The function of the tannins present in plants may thus be explained; if, for instance, phenols are formed by the oxidation of corresponding sugars,[1] the poisonous character of the former would be lessened by the introduction of the carbonic acid esters and subsequent coupling of the substances (depside formation). The depsides thus formed would serve as vehicle of the sugars and transport the migrating tannins,[2] and, after subsequent deposition of the sugars, would then be eliminated from the plant organism, either by oxidation into ellagic acid and phlobaphenes or by condensation with the formation of cork.

Diagrammatically, the following would represent the physiology of the tannins :—[3]

Sugar ⟶Phenol ⟶Hydroxybenzoic Acid   ⟶Depside

$$\longrightarrow \text{Migrating Depside} \longrightarrow \text{Glucoside} \longrightarrow \text{Free Depside} \longrightarrow \begin{cases} \text{Phlobaphene} \\ \text{Ellagic Acid} \\ \text{Cork.} \end{cases}$$
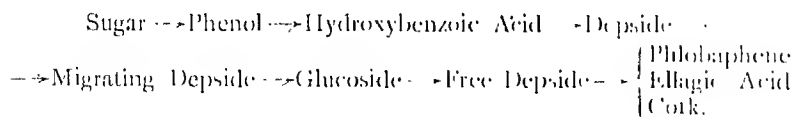
[1] Mielke, "Ueber die Stellung der Gerbstoffe im Stoffwechsel der Pflanzen" (Hamburg, 1893).

[2] Kraus, "Grundlinien zu einer Physiologie der Gerbstoffe" (1889).

[3] Nierenstein, "Chemie der Gerbstoffe" (Stuttgart, 1910).

CHART SHOWING THE DECOMPOSITION PRODUCTS OF TANNIN.

Pyrogallol
Metagallic acid
Carbonic acid

Dry
distillation

Tannin

Zinc
distillation

Dibenzymethane

Catechine

Hydrolysis

→ Protocatechuic acid

Gallic acid

Zn
distillation

→ Anthracene

H_2SO_4

Zn   distil-
lation

Rufigallic acid
(Hexoxyanthraquinone)

Oxida-   tion

Ellagic acid

Luteic acid

Sodium
amalgam

Alkaline
oxidation

Alizarin

Galloflavine

Cærulroellagic acid

Zn   distillation

Fluorene
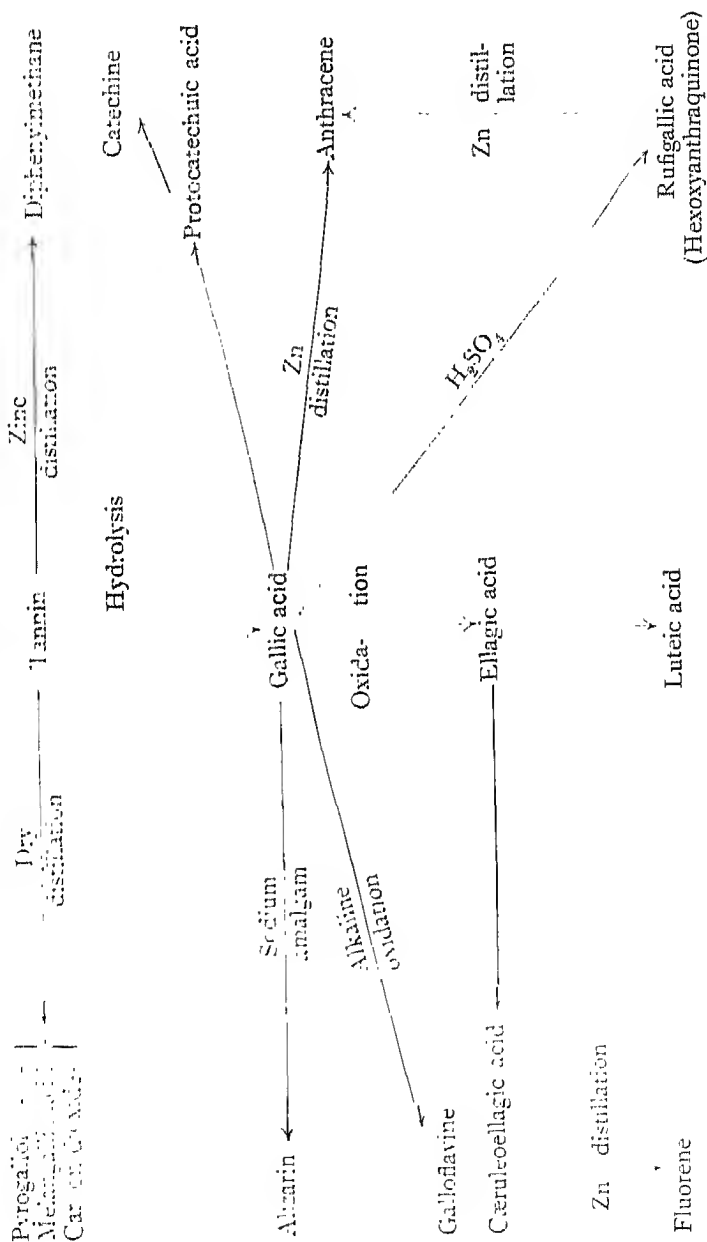
SYNTHESIS OF TANNING MATTERS

1. Aromatic Sulphonic Acids

In organic chemistry distinction is made between sulphonic acids of the aliphatic and the aromatic series, the characteristic group of these acids being the so-called *sulphonic acid group*, HSO_3.

When sulphides or mercaptans in glacial acetic acid solution are heated with permanganate, the resulting sulphonic acid compounds exhibit great similarity to compounds containing free carboxyl groups. The sulphonic acid group may also be directly introduced either by concentrated, or by fuming sulphuric acid, or by elimination of halogen by the action of sodium or silver sulphite on the halogen derivatives of the aliphatic compounds. Saturated hydrocarbons do not react with sulphur trioxide, but unsaturated hydrocarbons are readily attacked by SO_3. Similarly, halogenated compounds and alcohols react with concentrated or fuming sulphuric acid forming sulphonic and hydrosulphonic acids respectively. The aromatic compounds form, as a rule, sulphonic acids with much greater facility. Benzene, for instance, is easily converted into the *m*-disulphonic acid by gently heating with fuming sulphuric acid ; stronger heating converts the *m*- into the *p*-disulphonic acid, and at 190° C. the trisulphonic acid is formed. Toluene treated with fuming sulphuric acid first yields *o*- and *p*-sulphonic acids, finally *o*- and *p* disulphonic acids, ethylbenzene at the boiling point *p*-ethylbenzenesulphonic acid. Of the three isomeric xylenes *o*- and *m*-xylene dissolve in concentrated, *p*-xylene in fuming sulphuric acid only.

The action of sulphuric acid on naphthalene is stronger even than on benzene. Equal parts of naphthalene and sulphuric acid heated to 100° C. yield 80 per cent. *a*- and

20 per cent. β-monosulphonic acid. At 160°-170° C. 25 per cent. α- and 75 per cent. β-sulphonic acid is formed, and at higher temperatures β-monosulphonic acid only. If, on the other hand, 8 parts of naphthalene are heated with 3 parts of concentrated sulphuric acid to 186° C., two different naphthyldisulphonic acids are obtained.

Complete solution of the substance in sulphuric acid is, generally speaking, a criterion of complete sulphonation. A completely sulphonated compound should remain clear on dilution with water, or, in case precipitation occurs, the precipitate should be completely soluble in alkali or ammonia. It is necessary to submit the product to this test, since many organic substances are soluble in concentrated sulphuric acid without undergoing any alteration in composition.

Phosphoruspentoxide or potassium sulphate considerably increase the sulphonating property exhibited by fuming sulphuric acid.

The separation of the sulphonic acids from sulphuric acid is effected by salting out the former with common salt, or by removing the sulphuric acid with calcium, barium, or lead salts, provided that the sulphonic acid salts of these metals are soluble in water.

The sulphonic acid, in its chemically pure state, is best obtained from its crystalline barium salts, which are decomposed with the equivalent of sulphuric acid; another way is to decompose the calcium salts of the sulphonic acids with oxalic acid. The sulphonic acids are frequently hygroscopic and are easily soluble in water; the majority of their barium and lead salts are also soluble in water. The sulphonic acids are insoluble in ether. The halogens do not easily react with sulphonic acids, but when they do they usually replace the sulphonic acid group. In order to prepare the halogen substitution products, therefore, use is made of sulphonic chlorides. The latter are obtained by the action of chlorosulphonic acid on aromatic hydrocarbons; a simpler method, however, is to treat the dry alkali sulphonates with phosphorus pentachloride --

$$C_6H_5SO_3Na + PCl_5 = C_6H_5SO_2Cl + NaCl + POCl_3$$
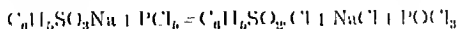
Derivatives of sulphonic chlorides are sulphonamides,

which are easily prepared from the former by grinding with ammonium carbonate—

$$C_6H_5SO_2.Cl + (NH_4)_2CO_3 = C_6H_5.SO_2.NH_2 + NH_4Cl + CO_2 + H_2O$$

Sulphonic chlorides react with alkaline sulphides to form thiosulphonic acids—

$$C_6H_5SO_2.Cl + K_2S = C_6H_5SO_2.SK + KCl$$
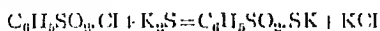
Sulphonic chlorides, dissolved in ether, yield sulphinic acids on reduction with zinc dust or metallic sodium—

$$C_6H_5SO_2.Cl + H_2 = C_6H_5SO_2.H + HCl$$
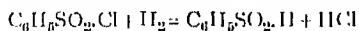
In the sulphonic acid compounds it is assumed that the sulphur is hexavalent, and it is hence possible to consider the sulphones to be esters of sulphinic acid.
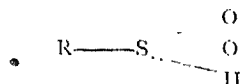
The sulphones are mostly solid bodies, which soften prior to melting when heated. They are very stable towards chemical reagents; for instance, saponification of a mono-sulphone very rarely yields sulphinic acid.

If a hydroxyl is substituted for a hydrogen atom in the aromatic hydrocarbons, the action of sulphuric acid is greatly facilitated; thus, by merely mixing phenol with sulphuric acid, the sulphonic acid is at once formed, whereby, in the cold, o-phenolsulphonic acid prevails which on heating for some time to 100°-110° C. is completely converted into p-phenolsulphonic acid. In the absence of free sulphuric acid the conversion of o- into p-phenolsulphonic acid is brought about by heating the aqueous solution. Phenol-2,4-disulphonic acid is prepared from o- or p-phenolsulphonic acid, whereas phenol-2,4,6-trisulphonic acid is prepared directly from phenol by heating with concentrated sulphuric acid in presence of phosphorus pentoxide. Phenolsulphonic acids are also obtained by fusing benzenedisulphonic acid with alkali.

Cresol is not so easily sulphonated as is phenol; o-cresol when heated eight to ten hours at 90° C. with one and one-

half times its weight of concentrated sulphuric acid, yields o-cresol-p-sulphonic acid.

The phenolsulphonic acids are strong, rather stable acids ; their alcoholic hydroxyl-hydrogen atom may, similarly to that of the phenols, be substituted by a metal or an alkyl radical.

From α- and β-naphthol a number of sulphonic acids may easily be prepared; viz., mono-, di-, and trisulphonic acids. Nearly all these acids are important as basic materials in the dyestuff industry, especially 2, 6-β-naphtholmonosulphonic acid (S-acid), 2, 3, 6-β-naphtholdisulphonic acid (R-acid) and 2, 6, 8-β-naphtholdisulphonic acid (G-acid).

2. Condensation of Phenols

Phenolsulphonic acids exhibit pronounced tendencies to condensation, for which purpose A. v. Baeyer (1872) employed aldehydes. The reaction is rather violent, and yields, in addition to well-defined crystalline substances, amorphous bodies resembling rosins. In addition to formaldehyde, paraformaldehyde, trioxymethylene, methylal, hexamethylenetetramine, and other substances containing a reactive methylene group, as well as acetaldehyde, benzaldehyde and other aldehydes may be employed to induce reaction.

A number of these condensation products are derivatives of diphenylamine or hydroxybenzyl alcohols. When the latter are heated, either by themselves or in presence of acids, anhydrides and polymerisation products are formed producing hard, brittle, fusible substances, insoluble in water but fairly soluble in organic solvents. The same substances are formed when phenols are condensed with formaldehyde, especially in the presence of acid contact substances and excess of phenol by sufficiently long heating at certain temperatures. The substances referred to are termed " Novolak " : similar to these are the so-called " Resols," insoluble and non-fusible substances, very resistant to chemical and physical action. Another member of the series is the so-called " Bakelite " or " Resitol," which does not fuse but softens when heated and swells in organic solvents. The ultimate product of this class of substances is " Resit " which is obtained when concentrated

hydrochloric acid is allowed to act upon a mixture of phenol and formaldehyde ; the temperature rises spontaneously, and a hard, porous, insoluble mass of great resistance is obtained. By heating resols, resitols are formed which, on further heating, are finally converted into resits.[1]

Of all these products, bakelite (resitol) has found the greatest industrial application ; in its purest form, this substance is a nearly colourless or light yellow body of sp. gr. 1.25 and, being a poor conductor of heat and electricity, constitutes an excellent insulating material; it is exceedingly resistant towards most chemical reagents even in concentrated forms of the latter. Its pronounced refractivity, and the ease with which it may be worked, makes bakelite a favourite substitute for amber (Ger. Pat., 286,568). Similarly, the resols which can be easily moulded are used either as such or mixed with sand, pulverised cork, asbestos or wood, and the moulded substances then converted into the more highly resistant bakelite by heating.

The constitution of these bodies no doubt depends largely on their method of preparation ; Baekeland[2] considers resit a polymerised hydroxybenzylmethylene glycol anhydride ; Raschig, a diphenylmethane derivative (e.g., dihydroxydiphenylmethane alcohol); Wohl[3] considers them polymerisation products of methylene derivatives of tautomeric phenol.

$$H_2C:C<\begin{matrix} CH \\ CH \end{matrix}\begin{matrix} CH \\ CH \end{matrix}>CO$$
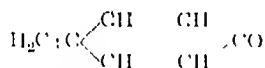
This group possesses the characteristic property of being capable of converting animal hide into leather when suitably dissolved. The author has dissolved a number of these water-insoluble condensation products in alkali and alcohol and was able to demonstrate their tanning effects on pelt ; bakelite is easily soluble in alkali ; a faintly alkaline solution partially precipitates gelatine, and completely so when the alkali is neutralised. This latter solution gives a dirty brown precipitate with iron salts.

[1] *Ber.*, 1892, 25, 3213.
[2] *Chem. Ztg.*, 1913, 73, 733.
[3] *Ber.*, 1912, 45, 2046.

These condensation products gained extraordinary importance for the tanning trade when Stiasny [1] succeeded in preparing them in water-soluble form when they are enabled to directly exert their tannoid properties. This may be done by acting upon two molecules of concentrated phenolsulphonic acid with one molecule of formaldehyde, the temperature thereby not exceeding 35° C. By condensation, however, considerable heat is liberated, and hence the rise in temperature can only be limited by adding the diluted formaldehyde drop by drop, whilst stirring and cooling, to the phenolsulphonic acid. The original letters patent is worded as follows : 10 kilos each of crude phenol and sulphuric acid (66° Bé.) are heated with stirring for two hours at 105°-106° C., cooled to about 35° C., and 4.63 kilos 30 per cent. formaldehyde added during three hours, the temperature thereby not exceeding 35° C.; the stirring is continued for a couple of hours after the final addition of formaldehyde. This yields about 24 kilos of the crude condensation product. On a commercial scale, however, cresol (cresylic acid) is substituted for phenol. There are three isomers of cresol, viz., o-, m-, and p-cresol, and it was naturally of interest to investigate whether one or the other of the isomers exerted any particular influence on the properties of the final product. It was found, however, that condensation products from the three isomers were distinguishable from one another neither in physical nor in tannoid properties. It is hence possible to employ crude cresol, which contains varying quantities of the o-, m- and p-compounds, in the manufacture of these tanning matters. [2]

The tar obtained from the Röchling coal-gas generator contains considerable quantities of phenols (B P. = 200°-250° C.), and the author has protected the use of these for the production of synthetic tannins by Ger. Pat., 262,558. A deep brown viscous mass is obtained which, when partly neutralised, yields similar results to those given by the product above referred to.

It may be anticipated that by analogy from the chemical reactions taking place in the condensation of phenols on the

[1] Ger. Pat., 262,558 ; Austr. Pat., 58,405.
[2] Ger. Pat., 291,457.

one hand and cresolsulphonic acid on the other, that all other homologues of phenol, its polyvalent derivatives, substitution products and acids, would yield similar condensation products.

The particular position occupied by the aromatic hydroxy compounds in the chemistry of substance possessing tannoid character is not only evidenced by the natural classification of the tannins, tannin derivatives, and decomposition products so far isolated and investigated, but also by other chemical behaviour shown by these substances. Meunier and Seyewetz,[1] for example, were able to show that phenol, p-aminophenol, chlorophenol, trinitrophenol, catechol, resorcinol, hydroquinone, monochlorohydroquinone, orcinol, pyrogallol, and gallotannic acid precipitate gelatine from its aqueous solution, that is, to a certain extent possess tanning properties.

The author has extended this series somewhat and obtained the following results :—

Substance.	Relative Behaviour Towards		
	Gelatine.	Hide Powder.	Pelt.
Tribromophenol [2]	Slight ppte.	Tans	Surface tannage
o-Nitrophenol	No ppte.	,,	,,
Br-o-Nitrophenol	Slight ppte.	,,	,,
Tribromopyrogallic acid	Ppte.	,,	,,
Bromophloroglucinol	,,	,,	No tannage
Galloflavine	Slight ppte.	,,	,,
Bromosalicylic acid	,,	,,	,,
Bromo-β-naphthol [2]	,,	,,	Tans
Rosolic acid [2]	,,	,,	,,
Gallic acid	No ppte.	No tannage	No tannage

By the condensation of their sulphonic acids, it may be demonstrated experimentally how the tannoid properties of nearly every member of the series are intensified. Investiga-

[1] *Collegium*, 1908, 313, 195.
[2] In alcoholic solution.

tion in this direction, however, has not been systematically undertaken, for which reason the author determined to examine this subject; but the enormous number of samples required, obtainable only with great difficulty during the war, made it impossible to conclude completely the researches in this field. What little has so far been done relatively to this subject should, when collected, indicate the way to be pursued in this wide field of investigation. What follows will hence comprise the conversion of a few of the most important members of this series of substances into their methylene-condensation products with a brief discussion of the quali-tative and tannoid reactions of the latter.

The didepside of phenolsulphonic acid is obtained by condensing carbomethoxyphenolsulphonic chloride with sodium phenolsulphonate in the presence of the calculated amount of caustic soda. A product of the composition

$$CH_3.O.COO.C_6H_4SO_2.O.C_6H_4.SO_3Na$$
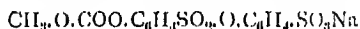
is first obtained, which on saponification with soda yields the pure didepside—

$$HO.C_6H_4.SO_2.C_6H_4.SO_3.Na$$
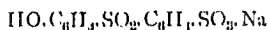
By acidifying the concentrated solution the didepside is obtained as a white crystalline substance; a solution of which precipitates gelatine without, however, exhibiting any tanning effect upon animal hide. If, on the other hand, the above ester is converted into the chloride

$$CH_3O.COO.C_6H_4SO_2.O.C_6H_4.SO_2Cl$$
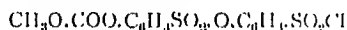
by treatment with PCl_5, and the chloride thus obtained further condensed with sodium phenolsulphonate, saponified, and the solution acidified, the pure tridepside

$$HO.C_6H_4.SO_2.O.C_6H_4.SO_2.O.C_6H_4.SO_3Na$$
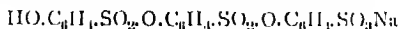
is precipitated as white crystalline needles which not only precipitate gelatine, but are capable of converting animal hide into leather.[1]

Of the class of hydroxy-cymenes *thymol*,

$$C_6H_3.CH_3.C_3H_7OH,$$
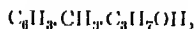
[1] *Chem. Ztg.*, 1919, 43, 318.

was converted into the water-soluble sulphonic acid by warming with concentrated sulphuric acid at 50° C., the sulphonic acid being subsequently easily condensed with formaldehyde by slightly heating the mixture. The condensation product thus obtained is a viscous brown mass which is easily soluble in water, precipitates gelatine completely, gives a bluish-black coloration with iron salts, and gives a precipitate with aniline hydrochloride. To investigate its tannoid properties, the mixture was brought to the acidity 1 gm = 10 c.c. N/10 NaOH and a piece of bated calf skin was then introduced into a solution measuring about 2° Bé. After eighteen hours the pelt was nearly tanned through, and a further twenty-four hours completed the tanning process, after which a light fat-liquor was given. The dried leather was brownish-grey in colour, possessed soft and full feel and good tensile strength.

On account of their importance, the three dihydroxy-benzenes were examined with a view to test their suitability for conversion into tannoid substances.

o-Dihydroxybenzene, catechol, yields a sulphonic acid easily soluble in water, which on the careful addition of formaldehyde assumes a blue colour. The compound thus obtained may be heated to 100° C., without depositing insolubles. A further addition of formaldehyde, however, results in the formation of a considerable quantity of insolubles whilst the liquid assumes a brown coloration. If, on the other hand, the sulphonic acid is diluted with twice its volume of water, formaldehyde added and the mixture heated on the water bath, the liquid immediately turns brown, the formaldehyde is completely fixed, and a condensation product soluble in water results. The latter gives a brownish-black coloration with ferric chloride, completely precipitates gelatine, but gives no opalescence with aniline hydrochloride. Tanning experiments with the partly neutralised (1 gm. = 10 c.c. N/10 NaOH) substance resulted in both grain and flesh being tanned with a black colour, whereas the interior of the pelt was pickled (white colour). After a further forty-eight hours, however, the black colour penetrated the pelt, and tannage was complete. The washed and lightly fat-liquored leather

was soft, of full feel and good tensile strength, and was greyish coloured throughout.

With regard to the black colour possessed by leathers tanned with synthetic tannins the following should be noted. When sulphonating and especially when condensing substances, black dyestuffs or very finely divided carbon in the colloidal state are often formed. Such a substance does not deposit the black particles, even when filtered through kaolin, and hence convert pelt into leather possessing black colour on the surface. The hide in this case acts as a perfect filtration medium, whereby the surface layers retaining the coloured particles assume their colour; thus only the pure tanning matter enters into the interior, which then, according to the composition of the former, imparts a colour varying from white to light brown to the inner layers.

m-Dihydroxybenzene, resorcinol, is also easily sulphonated by concentrated sulphuric acid, the brownish - coloured sulphonic acid being easily soluble in water. If the sulphonic acid is diluted with three times its volume of water, cooled down, a few drops of formaldehyde added and the mixture heated on the water bath to completely fix the formaldehyde, and this process repeated till no more formaldehyde is taken up, a brown water-soluble condensation product results, the aqueous solution of which precipitates gelatine completely, aniline hydrochloride only partly and which gives a deep blue colour with ferric chloride.

A piece of calf skin immersed in a solution of the partly neutralised (as above) product was tanned through in twenty-four hours; when lightly fat-liquored, the resulting leather possessed a yellowish-green colour and good tensile strength, and was soft and full.

p-Dihydroxybenzene, hydroquinone, was converted into the water-soluble sulphonic acid by heating it with concentrated sulphuric acid at 100° C.; the sulphonic acid, mixed with formaldehyde at ordinary temperature, immediately solidifies to a white mass, which is soluble in water and which had completely fixed the formaldehyde. If, however, this mass is heated for some time to 100° C., it assumes a light brown coloration and its solubility in water is diminished.

A slight excess of formaldehyde and the application of heat result in dark violet insoluble condensation products. The aqueous solution precipitates gelatine, gives a deep blue colour with ferric chloride, but gives no precipitate with aniline hydrochloride; on the other hand, addition of potassium nitrite produces the yellow colour characteristic of hydroquinone.

The product effects a slower tannage (seven days) than the former product, when a brown, soft, but rather empty leather of good tensile strength is obtained.

Of the *trihydroxybenzenes* pyrogallol and phloroglucinol only were included in these investigations.

When pyrogallol is sulphonated with concentrated sulphuric acid a violet-coloured sulphonic acid, soluble in water, is obtained, which, when treated with formaldehyde first in the cold and then when heated, yields a solid deep red-coloured mass, which precipitates gelatine but not aniline hydrochloride, and gives a blackish-brown colour with ferric chloride. The partly neutralised substance in aqueous solution tans pelt in twenty-four hours with black colour on the surface only, the intermediary layer being pickled (white colour) only, but the black-coloured tanning matter ultimately penetrates the pelt, which tanned through in seven days. The resultant leather is coloured black throughout, is full, soft, and possesses good tensile strength.

Sulphonation of phloroglucinol succeeds at higher temperatures only, the sulphonic acid being a solid which is scarcely soluble in water, the latter then assuming a wine-red colour. The condensation product prepared as described for resorcinol, but requiring higher temperature—is a brick-red powder, insoluble in water.

The same end-product also seems to be obtained by simply heating the sulphonic acid at a higher temperature; this also induces condensation with the formation of a reddish-brown mass insoluble in water. It is, of course, impossible to attempt any tanning experiments with this product in aqueous solution; attempts at dissolving the condensation product in alcohol proved barren of result, since only traces of impurities accompanying the substance

dissolved, imparting a light reddish-brown colour to the solution. In highly concentrated alcohol, however, the condensation product is somewhat soluble, yielding a reddish-brown solution. A piece of pelt introduced into the alcoholic solution was surface tanned only after forty-eight hours, leaving the remainder of the pelt pickled ; extending the experiment over a further four days produced no change in the pelt. The latter was therefore rinsed with water, lightly fat-liquored and dried, when a soft but empty leather of grey colour and good tensile strength was obtained. It appears, therefore, to be a case of pseudo-tannage, where an infinitesimal amount of synthetic tannin produces a tanning effect without, however, a true tannage being effected.

The Elberfelder Farbenfabriken have protected the use of the condensation products of di- and polyhydroxybenzenes by Ger. Pat., 282,313 ; owing to the high cost of the latter substances, however, it is doubtful whether synthetic tannins prepared from these materials would not be too expensive for any other than pharmaceutical purposes.

Before leaving the phenols, mention must be made of the quinones, the use of which for tanning purposes was first protected by Ger. Pat., 206,957 (30th April 1907). According to this patent, only 400 gm. of quinone are required for the conversion into leather of 400 kilos pelt, drum tannage being preferable. During the process the leather first assumes a reddish colour, changing through violet to brown ; its resistance to water, acids, and alkalies is said to be considerably greater than that exhibited by all other kinds of leather.

The chemistry of the quinone tannage has been investigated, and an explanation given by Thuau [1] assumes a reaction between the quinone and the amino groups of the hide protein with the formation of hydroquinone—

$$2R.NH_2 + 2C_6H_4\!\!<\!\!{O \atop O} = C_6H_4\!\!<\!\!{OH \atop OH} + C_6H_4(O.NH.R)_2$$

(Pelt.)   (Leather.)
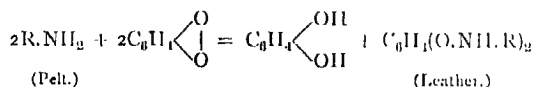
[1] *Collegium*, 1909, 363, 211.

Fahrion has shown that, during the tanning process, the quinone loses its active oxygen, and this can only be brought about by the amino group of the hide protein, the amino group only being capable of effecting reduction of the quinone. An analogy is here offered by dianilinoquinone. A spent quinone liquor contains considerable amounts of hydroquinone. The tannage may also be effected by exposing pelt saturated with hydroquinone to oxidation by the air. The pelt, which is unaltered by the hydroquinone bath, on being removed from the latter, and in the presence of alkali, assumes a red colour at first, which changes into violet, blue, and finally brown, the pelt being thereby converted into a quinone-tanned leather.

It may be noted that quinone only effects pseudo-tannage ; quinone mixed with water deposits, in time, a black amorphous substance practically insoluble in water. This substance is easily adsorbed by hide powder, but is not capable of converting the latter into that insoluble form into which it is converted by the natural tannins.

Amongst polyhydric alcohols, the behaviour of the methyl ester of catechol, *guaiacol*, was investigated. The sulphonic acid was prepared by heating guaiacol with concentrated sulphuric acid, the resulting water-soluble product possessing a light, brownish-green colour. On condensing the sulphonic acid with formaldehyde, the same precautions were observed as in the case of resorcinol, but complete fixation of the formaldehyde could only be obtained by finally heating the product for a short time over a free flame, at about 105° C. Condensation was indicated by the brownish appearance of the liquid. No insoluble products were formed. The condensation product easily dissolves in water, the solution assuming a rich brown colour and exhibiting the following reactions : gelatine is completely precipitated, aniline hydrochloride produces opalescence, and ferric chloride a deep brown coloration.

Tannage, with the partly neutralised product, was rapid, the pelt being nearly tanned through in twenty-four hours, excepting a small white streak in the middle ; after a further twenty-four hours this streak had vanished, and the completely

tanned, dark grey-coloured leather, after washing, fat-liquoring, and drying, was soft, full, and of good tensile strength, very similar to the leather yielded by the catechol-condensation product.

Of the nitro-compounds, trinitrophenol, $C_6H_2(NO_2)_3.OH$ (picric acid), was investigated. If a concentrated solution of picric acid is brought into contact with pelt it will penetrate the latter completely in a few days; it is, however, difficult to fat-liquor the resultant leather, since the fat is absorbed only with difficulty. If a pelt treated in this way be dried, a soft but rather flat leather results, the colour of which easily rubs off, the leather also tasting intensely bitter. These disagreeable qualities prevent a general use of this material for tanning purposes; in spite of them, however, picric acid, in admixture with boracic acid, salicylic acid, and glycerol, is used in the production of the so-called transparent leather. The latter is very flexible and possesses great tensile strength, but loses the latter quality when exposed to heat, and, when stored, also loses its flexibility. By simply washing with water, the leather is reconverted into pelt.

When picric acid is treated with hot sulphuric acid and formaldehyde gradually added, a dark coloured water-soluble condensation product is formed which strongly precipitates gelatine. Exposed to the action of bromine, the condensation product yields a mass which is insoluble in water.

Experience has taught that the amino bodies - the basic N-derivatives of the phenols—do not yield substances possessing tannoid properties on condensation. On account of their importance, however, a few have been included in this series of investigations.

Aminobenzene, $C_6H_5.NH_2$, aniline, treated with sulphuric acid, yields the water-soluble aniline sulphate, which, on cautious addition of formaldehyde, yields a reddish-coloured gel, insoluble in water, in addition to a small volume of a reddish-yellow liquid. The latter precipitates gelatine, but is not capable of converting pelt into leather. The insoluble gel is likewise insoluble in alcohol, so that tanning experiments with this substance are excluded.

Dimethylaniline, $C_6H_5.N(CH_3)_2$, when treated with sulphuric acid, yields a product soluble in water which neither reacts with nor fixes formaldehyde. Hence the substance does not precipitate gelatine.

If, on the other hand, nitrosodimethylaniline,

$$C_6H_4<^{NO}_{(CH_3)_2}$$
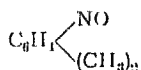
is sulphonated, and the water-soluble sulphonation product heated with formaldehyde for some time, the product remains soluble in water and precipitates gelatine. No tanning effect could, however, be detected.

Arylsulphaminoarylsulphonic acids and arylsulphoxyarylsulphonic acids precipitate gelatine, but are devoid of tannoid character. The latter is acquired by compounds belonging to this class containing two or more sulphamino groups, or when they, in addition to one sulphamino group, contain a sulphoxy group and another sulphonic group. According to Ger. Pat., 297,187 (Society of Chemical Industry, Basle), such compounds are obtained when, for instance, sodium sulphanilide in alkaline solution acts upon nitro toluenesulphochloride, and the resulting nitrotoluene sulphamino compound is subsequently reduced with acetic acid and iron. The resulting aminotoluenesulphamino benzenesulphonic acid is finally treated with p-toluene-sulphonic chloride till the latter disappears. A compound of the composition
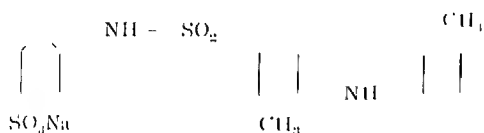
is thereby obtained, which, when acidified, is readily capable of being used for tanning purposes.

The intermediary product of the aminotoluenesulphamino benzenesulphonic acid obtained by this process may again be employed for the purpose of reacting with one-half molecule

4

soda and 1 molecule nitrotoluenesulphonic chloride. The following compound is obtained—
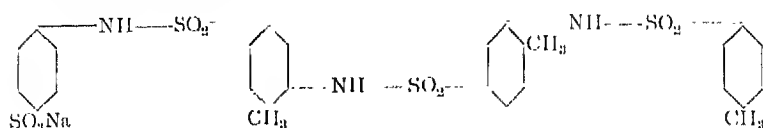
If *p*-toluenesulphaminobenzenesulphonic chloride is condensed with sodium sulphanilide, a compound,
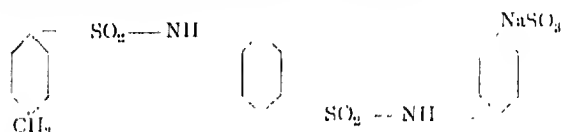
is obtained which, when acidified, exhibits tannoid properties.

On condensing sodium phenolsulphonate with nitrotoluenesulphonic chloride, reducing the condensation product and condensing the latter with *p*-toluenesulphonic chloride, a compound similar to the above is obtained—
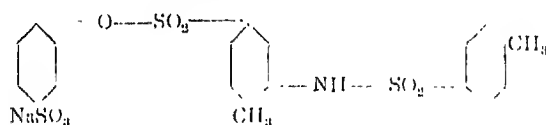
Again, a similar product is obtained when *p*-toluenesulphaminobenzenesulphonic chloride or its homologues or isomers are condensed with sodium-*o*-cresylsulphonate—

The chloride of this compound may again be condensed, for instance, with sodium aminotoluenesulphaminobenzenesulphonate, and yields the compound—
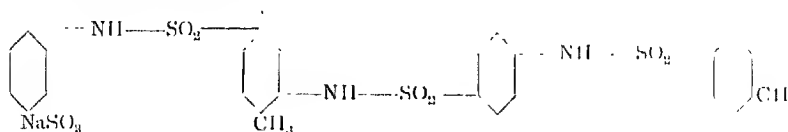
The three latter compounds, when dissolved in water and the solution acidified, exert tanning action.

It is also possible to employ mixtures of arylsulphamino-benzylsulphonic acids in acidified aqueous solution for tanning purposes. According to Ger. Pat., 297,188, such mixtures are obtained by nitrating benzylchloride and heating with an equimolecular amount of sodium sulphite ; the sodium nitro-benzylsulphonate thus obtained is reduced to aminobenzyl-sulphonic acid with iron and acetic acid, and finally condensed with the calculated amount of *p*-toluenesulphonic chloride. A mixture *o*- and *p*-toluenesulphaminobenzylsulphonic acid [1] thus results.

Amongst *aromatic alcohols* the dihydric alcohols show characteristic behaviour ; the latter combine with sulphonic acids with the elimination of water, condensation taking place without formaldehyde, and the resulting products being soluble in water and possessing tannoid properties.[2] In addition to phenolic mono- and disulphonic acids (and higher sulphonation compounds), the homologues, cresols, xylenols, and naphthols enter into reaction. The two components condense with great ease, liberating heat ; dilute solutions (of the components) are heated to about 100° C., the process being complete in a few minutes. The products obtained are exceedingly pure and are easily crystallisable. Employing 1, respectively 2, molecules of sulphonic acid, the reactions take place according to :—

[1] *Cf.* also Ger. Pat., 319,713 and 320,613.
[2] Ger. Pat., 300,567, of 20th September 1917.

$$\frac{OH}{HSO_3}\!\!\Big\rangle C_6H_4 + HO.C_6H_3\!\!\Big\langle\frac{CH_2.OH}{CH_2.OH} = H_2O + \frac{OH}{HSO_3}\!\!\Big\rangle C_6H_3 - CH_2 - C_6H_3\!\!\Big\langle\frac{OH}{CH_2.OH}$$

2.
$$\frac{OH}{HSO_3}\!\!\Big\rangle C_6H_4 - HO.C_6H_3\!\!\Big\langle\frac{CH_2.OH}{CH_2.OH} = 2H_2O + HO.C_6H_3\!\!\Big\langle\frac{CH_2.C_6H_3\diagdown^{OH}_{HSO_3}}{CH_2.C_6H_3\diagdown^{OH}_{HSO_3}}$$

$$\frac{OH}{HSO_3}\!\!\Big\rangle C_6H_3.CH_2 - HO.C_6H_3\!\!\Big\langle\frac{CH_2.OH}{CH_2.OH} = H_2O + \frac{OH}{HSO_3}\!\!\Big\rangle C_6H_2.CH_2.CH_2.C_6H_3\!\!\Big\langle\frac{OH}{CH_2.OH}$$

2.
$$\frac{OH}{HSO_3}\!\!\Big\rangle C_6H_3.CH_2 - HO.C_6H_3\!\!\Big\langle\frac{CH_2.OH}{CH_2.OH} = 2H_2O + HO.C_6H_3\!\!\Big\langle\frac{CH_2.C_6H_3.CH_2\diagdown^{OH}_{HSO_3}}{CH_2.C_6H_3.CH_2\diagdown^{OH}_{HSO_3}}$$

$$\frac{OH}{HSO_3}\!\!\Big\rangle C_{10}H_5 - HO.C_5H \cdot \frac{CH_2.OH}{CH_2.OH} = H_2O + \frac{HO}{HSO_3}\!\!\Big\rangle C_{10}H_5.CH_2.C_5H_3\!\!\Big\langle\frac{OH}{CH_2.OH}$$

2.
$$\frac{OH}{HSO_3}\!\!\Big\rangle C_{10}H_5 - HO.C_5H \cdot \frac{CH_2.OH}{CH_2.OH} = 2H_2O + HO.C_6H_3\!\!\Big\langle\frac{CH_2.C_{10}H_5\diagdown^{OH}_{HSO_3}}{CH_2.C_{10}H_5\diagdown^{OH}_{HSO_3}}$$

The condensation products above enumerated were tested with regard to their tanning power, both non-neutralised and partly neutralised (1 : 10, 1 : 20, and 1 : 30 c.c. N/10 NaOH) samples being examined. In all cases rapid tannage was observed yielding firm and soft leathers of light brown colour and varying degrees of swollenness.

Relatively to their reactions, all the products strongly precipitate gelatine, whereas only the condensation products of phenol, cresol, and xylenol derivatives give a characteristic coloration with iron salts.

The tannin contents of the non-neutralised condensation products lie between 72-80 per cent.—figures which clearly indicate the purity and efficiency of these substances.

Notable amongst *aromatic acids* is salicylic acid, $C_6H_4.OH.COOH$, which at higher temperatures is easily sulphonated with concentrated sulphuric acid ; the sulphonation product represents a white solid, which easily dissolves in water forming a clear liquid. The sulphonic acid, when mixed with about one-third of its weight of water and heated to about 120° C., is easily condensed with formaldehyde. Towards the end of the reaction, considerable frothing sets in, but in spite of the high temperature required by this reaction no insoluble bakelites are formed. A reddish-brown fluid is obtained easily soluble in water, to which it imparts a brown colour. An aqueous solution of the product completely precipitates gelatine, gives a strong opalescence with aniline hydrochloride and a deep violet coloration with ferric chloride. Neutralised as usual, the product, in a 3° Bé. solution, converts pelt within three days into a white, full leather of good tensile strength.

This process has been patented by the Deutsch-Koloniale Gerb und Farbstoff Gesellschaft (German-Colonial Tanning and Colour Extracts Ltd.) in Karlsruhe, the letters patent also including the ring homologues of salicylic acid. Similar results are obtained when cresotinic acid (hydroxy-toluic acid), $OH.C_6H_3.CH_3.COOH$, is employed as base.

If the phenyl ester of salicylic acid, *Salol*,

$$HO.C_6H_4.CO.O.C_6H_5,$$
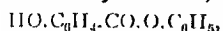
is sulphonated, a product is obtained which is easily soluble

in water, but which is identified as a mixture of the sulphonation products of salicylic acid and phenol, the salol being dissociated on sulphonation. The temperature must not exceed 80° C. by condensation with formaldehyde, or insoluble bakelite will be formed from the phenol; the aldehyde must also be added gradually. An aqueous solution of the partly neutralised condensation product has a pronounced tanning effect on pelt, and converts the latter into leather in one to two days; the leather being very similar to that produced by the salicylic acid condensation product. The qualitative reactions of the product in aqueous solution are the same as those given by the salicylic acid condensation product.

Salicylic acid may, however, also be condensed with formaldehyde without first being sulphonated; in this case, a little hydrochloric acid should be present. A product slightly soluble in water is obtained, which may be looked upon as being methylenedisalicylic acid. In alkaline solution it is easily soluble,[1] the liquid possessing an intensely bitter taste. The sodium salt gives a deep violet coloration with ferric chloride, a slight precipitate with gelatine, and slight opalescence with aniline hydrochloride. In contact with pelt, however, it exhibits no tanning effect, but when dissolved in alcohol, a pickling effect may be observed.[2]

The attempt at preparing a condensation product from sodium-*m*-hydroxybenzoate by means of formaldehyde and bisulphite is worthy of attention. A dark brown, viscous liquid is obtained which is perfectly soluble in water, and the aqueous solution of which gives opalescence with gelatine, a precipitate with aniline hydrochloride, and a bluish-black coloration with ferric chloride. Its behaviour towards pelt is very similar to that of phenolsulphonic acid, and it yields a similar leather.

A very similar condensation product was obtained by condensing sodium-*p*-hydroxybenzoate with formaldehyde and

[1] Its solubility in alcohol and alkalies renders this product an effective and cheap substitute for shellac. – *Transl.*

[2] A similar reaction is observable in the case of the sodium salts of METHYLENEDISALICYLIC acid brominated or iodised, which form a clear solution varying from red to reddish-brown.

subsequent sulphonation with sulphuric acid. From a practical standpoint, however, these substances cannot be employed, since their tanning action is only effective in acid solutions of such concentration of acid as would gelatinise the pelt.

If, on the other hand, non-condensed methane derivatives of phenol, e.g., hydroxyphenylmethanesulphonic acid, are partly neutralised and a solution of the product thus obtained used for tanning experiments, no tanning action is observable. The acidified solution does not precipitate gelatine, and gives a dark brown coloration only with ferric chloride.

Gallic Acid, $C_6H_2(OH)_3COOH$, when heated with sulphuric acid, is easily converted into the insoluble rufigallic acid, which is also insoluble in alcohol. If, however, gallic acid is heated with an excess of sulphuric acid, the product cooled and treated with formaldehyde, a deep brown condensation product is obtained which is soluble in alcohol, and in this state is capable of converting pelt into a substance similar to leather which, though rather hard, possesses good tensile strength. This water-insoluble condensation product is also soluble in alkalies, the solution exhibiting properties similar to that described above. Gallic acid, therefore, is not a suitable base for the production of synthetic tannins soluble in water.

Phthalic acid also is difficult to sulphonate: the sulphonated compound treated with formaldehyde gives only water-insoluble condensation products.

3. Condensation of Naphthalene Derivatives

The simplest method of condensing β-naphthalenesulphonic acid is to heat it at 135° C. at a pressure of 20 mm. for several hours.[1] The resulting product is a cheesy mass which reacts strongly acid. By reducing the acidity of the substance to 1 gm. = 10 c.c. N/10 NaOH, a grey, cheesy mass results, which easily dissolves in water, the solution being coloured a light yellow-brown and precipitating gelatine aniline hydrochloride; no coloration, however, appears on adding ferric chloride.

The condensation of β-naphthalenesulphonic acid, how-

[1] Austr. Pat., 61,061, of 10th September 1913.

ever, proceeds with much greater energy in the presence of formaldehyde. In practice, for instance, 10 kilos of naphthalene is heated with the same weight of concentrated sulphuric acid (66° Bé.), when the mixture is converted into β-naphthalenesulphonic acid by heating for several hours at 150°-160° C.; the sulphonation completed, the sulphonic acid is cooled to about 85° C., and 4 kilos of formaldehyde (30 per cent. by weight) slowly added ; finally, the product is stirred at the temperature mentioned till all formaldehyde has combined.[1]

Tanning experiments with this product yielded, in a short time, a nearly white coloured leather (see later).

In addition to formaldehyde, there are other substances which induce condensation of naphthalenesulphonic acid ; if, for instance, sulphur chloride is allowed to act upon β-naphthalenesulphonic acid, a light brown solid of pronounced acidic character is obtained ; if the latter is partly neutralised with caustic soda, a greyish-brown solid results, which dissolves in water with a light brown colour, the solution precipitating gelatine and aniline hydrochloride, but giving no coloration with ferric chloride.[2]

Tanning experiments with this product in aqueous solution gave a light brown, rather soft leather, and this, in addition to the qualitative reactions of the substance, prove that this method of condensation hardly alters the character of the product from a tanning point of view. The brown coloration imparted to the leather tanned with this condensation product owes its existence to coloured intermediary products.

Attempts at condensing chloronaphthalenesulphonic acid and nitronaphthalenesulphonic acid resulted in soluble condensation products which gave some of the reactions given by the tannins (precipitation of gelatine and aniline hydrochloride), but which were incapable of tanning pelt, a light tannage being effected on the surface only.

α-Naphthol dissolved in hot concentrated sulphuric acid and heated for some time on the water bath, yields the light brown, water-soluble α-naphtholsulphonic acid. A dilute

[1] Austr. Pat., 69,194, of 25th June 1915 ; Ger. Pat., 290,965.
[2] Austr. Pat., 96,194.

solution of the latter, when treated with formaldehyde in the cold, undergoes no change; on heating the mixture on the water bath a brown precipitate is thrown down.   If gelatine solution is added to the opaque liquid, a yellow flocculent precipitate separates.   If caustic soda is added to the opaque liquid containing the condensation product described above, a clear solution results from which no deposit separates on the addition of acetic acid.   Gelatine is precipitated by this solution.

The concentrated hot α-naphtholsulphonic acid, upon addition of sufficient formaldehyde, effervesces strongly and yields a dark brown condensation product insoluble in water, but soluble in caustic soda.   If acetic acid is added in excess to the alkaline solution, the resultant solution strongly precipitates gelatine.

A suspension in water of the insoluble condensation product does not precipitate gelatine.

β-Naphthol, dissolved in hot concentrated sulphuric acid and heated for some time, yields the light brown, viscous β-naphtholsulphonic acid.   A dilute solution of the latter, mixed with formaldehyde, remains clear; when heated on the water bath, however, it assumes a dark, reddish-yellow colour, and remains soluble in water and precipitates gelatine strongly.   This condensation product, on adding excess of caustic soda, assumes a deep blue coloration, the alkaline solution giving no precipitate with gelatine; on adding acetic acid the solution turns brown, remains clear, and now precipitates gelatine.

The concentrated β-naphtholsulphonic acid heated with formaldehyde on the water bath yields as condensation product a dark, reddish-yellow mass, soluble in water, which precipitates gelatine.   A dilute solution, when allowed to act upon pelt, gave in a few days a light brown leather, the properties of which are very similar to those possessed by vegetable tanned leathers.

The use of naphtholsulphonic and aminonaphtholsulphonic acids for the manufacture of synthetic tannins is protected by Ger. Pats., 293,640, 293,693, 293,042, and 303,640.[1]

[1] *Cf.* Austr. Pat., 70,162.

It is a remarkable fact that non-condensed methane derivatives of naphthol, *e.g.*, β-naphthol-α-methanesulphonic acid, dissolved in water and partly neutralised, are devoid of tanning character when allowed to act upon pelt. Neither does this substance precipitate gelatine, but it does give a deep blue coloration with ferric chloride.

The condensation product of β-naphthol above referred to precipitates gelatine and aniline hydrochloride and gives a brown coloration with ferric chloride.

Thionaphtholsulphonic acid, when acted upon by formaldehyde, yields a condensation product of the following constitution :—
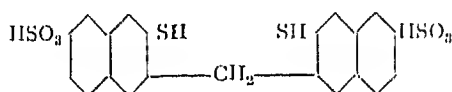
This is a light yellow powder which, dissolved in water, yields an opaque solution ; the latter only exhibits any tanning properties when it is not neutralised and even slightly acidified and then precipitates gelatine, aniline hydrochloride and barium chloride ; dissolved in alkali, it forms a clear, yellow solution devoid of tannoid properties. Leather tanned with the acidified solution is very similar to those tanned with the phenolsulphonic acid condensation products ; its colour, however, is more pronouncedly yellow.

β-Naphthol condensed with hydrochloric acid and formaldehyde yields a methylenedinaphthol, which is insoluble in water ; the sodium salt, however, easily dissolves. The same condensation, however, takes place in alkaline solution with direct formation of the sodium salt. The condensation product gives a slight precipitate with gelatine, and a bluish-grey precipitate with ferric chloride ; acids re-precipitate the insoluble methylene compound. Towards pelt it exhibits tanning properties, whereby the insoluble product referred to above is deposited, and soft, full, and white leather is obtained, possessing, however, but little tensile strength.

4. Condensation Products of the Anthracene Group

Anthracene heated with excess sulphuric acid yields the water-soluble anthracenesulphonic acid ; the latter, when heated with formaldehyde, yields water-soluble, reddish-brown condensation products, which remain soluble on prolonged heating with formaldehyde. The aqueous solution of the condensation product shows no particular reactions ; it gives a flocculent precipitate with gelatine and a green precipitate with copper sulphate, soluble with blue colour in excess of the reagent.

The partly neutralised solution tans pelt—to which it imparts a brown colour—in eight days, but on the surface only ; the inner layers are merely pseudo-tanned (white colour). When dried, pelt thus treated yields a full and soft leather with brown grain and flesh possessing but little tensile strength. Hence, this condensation product exerts a pickling rather than a tanning effect.

Anthraquinone heated with sulphuric acid and treated with formaldehyde in the usual manner, yields a substance which, when mixed with water, forms an opaque, milky solution. This is not altered by excess of caustic soda. The aqueous solution precipitates gelatine and aniline hydrochloride ; all other tannin reagents give no reaction.

The partly neutralised solution of the condensation product exerts, in the main, a pickling action on pelt ; only the surface of which is tanned, with brown colour, the remainder being merely pickled (white colour). During "tannage," bakelite is formed in the liquid, and practically all solubles originally present are deposited. The tannage completed, a light brown, fairly soft and full leather, possessing little tensile strength, results ; this leather can be washed only with great difficulty and approaches more the character of a pickled pelt.

1-Hydroxyanthraquinone, 1,5-dichloroanthraquinone, 1,5-diaminoanthraquinone, 1-methylaminoanthraquinone, 1-benzoylamino, 6-chloranthraquinone, 1-m-toluidoanthraquinone, when treated with sulphuric acid and formaldehyde, all yield condensation products which are but little soluble in
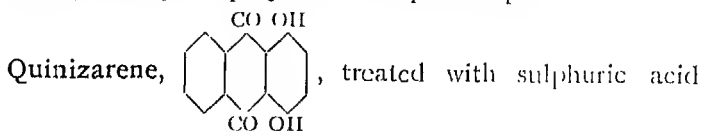
water, and which do not at all precipitate gelatine. Tanning experiments with these condensation products in alcoholic solution yielded empty leathers of pronounced pickle character.

If, however, 1-methylamino-4-bromanthraquinone is condensed with sulphuric acid and formaldehyde, a condensation product is obtained which is but slightly soluble in water, but which precipitates gelatine.

When **phenanthrequinone** is heated with excess of sulphuric acid for some time, a water-soluble, reddish-yellow coloured condensation product results. The latter, when treated with formaldehyde in the cold and then finally heated, gradually fixes the formaldehyde and forms a substance soluble in water. If the heating, however, is prolonged, insoluble bakelites are formed, which are neither soluble in alkali nor in alcohol.

An aqueous solution of these condensation products gives no reactions with the usual tannin reagents, though it completely precipitates gelatine. When acting upon pelt, the partly neutralised dilute solution of the condensation product pickles the former, and after a few days the pelt is converted into a light brown, full, and rather soft leather possessing good tensile strength.

When the condensation product is acted upon by bromine in hot aqueous solution, an additive compound is formed and the resulting product is soluble in water. The aqueous solution of the brominated product gives no special reactions with the usual tannin reagents, but precipitates gelatine completely. Its tanning action upon pelt is much slower than that of the original condensation product; the surface of the pelt only is tanned with brown colour, the inner pelt being only pickled (light brown colour). When dried, a hard and empty leather of good tensile strength is obtained, possessing mainly the properties of a pickled pelt.

Quinizarene, , treated with sulphuric acid

and formaldehyde, yields a condensation product which is

but little soluble in water and which does not precipitate gelatine.

Quinoline, when sulphonated and condensed with formaldehyde, yields a dark coloured condensation product, completely soluble in water ; the solution does not precipitate gelatine.

Oxyquinoline exhibits similar behaviour.

On the other hand, the use of *retene* (methylisopropyl-phenanthrene),
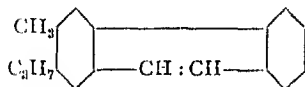
for the production of synthetic tannins, is protected by Ger. Pat., 290,965.[1]

5. Di- and Triphenylmethane Group

If **diphenylmethane,** $(C_6H_5)_2CH_2$, is heated with excess sulphuric acid, a dark blue mass, easily soluble in water, is obtained. The product gently heated with formaldehyde yields a brown, water-soluble condensation product ; once condensation is complete, the product will stand stronger heat. If, on the other hand, more formaldehyde is added, brown, water-insoluble bakelites are formed. The water-soluble condensation product precipitates gelatine, but not aniline hydrochloride. Dissolved in water, it possesses tannoid properties : the pelt is, however, tanned on the surface only, the intermediary layers being merely pickled ; after four days in the solution, the pelt after drying was found to be converted into a greyish-brown, badly coloured leather, which was empty, hard, and possessed but little tensile strength.

Carbazole (dibenzopyrrole),

on the other hand, was found a suitable base for the commercial production of synthetic tannins ; its use is protected by Ger. Pat., 290,965.

[1] *Cf.* Austr. Pat., 69,194.

Triphenylmethane, $(C_6H_5)_3CH$, heated with excess sulphuric acid, yields a nearly black mass which, when condensed with formaldehyde in the cold, and subsequently heated, yields a mass which is soluble in water. With gelatine and aniline hydrochloride it exhibits reactions similar to those given by the diphenylmethane condensation products; its tanning properties also are similar to those of the latter. The resultant leather is black, but is soft and full and possesses good tensile strength.

Baeyer's observation,[1] that pyrogallol on condensation with formaldehyde yields an amorphous body soluble in water, which precipitates gelatine and is very similar to tannin, was confirmed by Caro[2] and Kahl.[3] These investigators found that by the condensation of phenols and hydroxybenzoic acids with formaldehyde, diphenylmethane derivatives were formed; pyrogallol yields hexahydroxydiphenylmethane—

$$CH_2 \left< \begin{array}{l} C_6H_2(OH)_3 \\ C_6H_2(OH)_3 \end{array} \right.$$
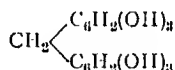
Nierenstein[4] repeated these experiments, and found that in addition to the insoluble diphenylmethanes water-soluble bodies were formed, which latter precipitate gelatine. The condensation product yielded by gallic acid was identified as hexahydroxyaurinecarboxylic acid—

$$C \left< \begin{array}{l} C_6H(OH)_3.COOH \\ C_6H(OH)_3.COOH \\ C_6H(OH)_3.COOH \end{array} \right| O$$
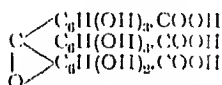
which is formed in addition to hexahydroxydiphenylmethanedicarboxylic acid—

$$CH_2 \left< \begin{array}{l} C_6H(OH)_3.COOH \\ C_6H(OH)_3.COOH \end{array} \right.$$
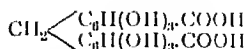
Baeyer's experiment with pyrogallol probably also yields,

[1] *Ber.*, 1872, 5, 280, 1096.

[2] *Ibid.*, 1892, 25, 947.

[3] *Ibid.*, 1898, 31, 114.

[4] *Collegium*, 1905, 221.

according to Nierenstein, another compound of the following constitution—

$$C \begin{cases} C_6H_2(OH)_3 \\ C_6H_2(OH)_3 \\ C_6H_2(OH)_3 \end{cases}$$
$$|$$
$$O$$
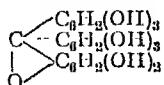
Nierenstein considers these bodies confirmation of his hypothesis of the existence of a " tannophor," —CO—, in the tannins.

This supposition was adopted by Stiasny[1] and Kauschke,[2] and the latter points out that these easily soluble substances exhibit tanning properties.   Nierenstein[3] was further able to show that by all processes of condensation between phenols (or hydroxybenzoic acids) and formaldehyde, compounds of the character of hydroxyaurine (or hydroxyaurinecarboxylic acid) were formed in addition to the insoluble hydroxy-diphenylmethanes (or hydroxydiphenylmethanecarboxylic acids), the former possessing the characteristic tannophor group and hence precipitating gelatine, *i.e.*, exerting tanning action.   If the formation of leather is viewed in the light of Schiff's base,[4] one may consider the constitution of a hexa-hydroxyaurinecarboxylic acid leather as follows :—

$$C \begin{cases} C_6H(OH)_3.COOH \\ C_6H(OH)_3.COOH \\ C_6H(OH)_3.COOH \end{cases}$$
$$|$$
$$R—N$$
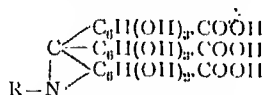
In the preparation of these and similar condensation products, Nierenstein and Webster[5] observed a peculiar steric effect of the carboxyl group.   Each 2.5 gm. of the phenol or the acid in question were dissolved in 30 c.c. of water, the solution brought to boil and 5 c.c. formaldehyde (20 per cent.) and 2.5 c.c. hydrochloric acid added drop by drop ; the precipitate formed was filtered off after twenty-four hours, dried at 110° C. to constant weight, extracted (in a Gooch crucible) freely with water, and the residue again

[1] *Gerber*, 1905, 233.
[2] *Collegium*, 1906, 362.
[3] *Ibid.*, 1906, 434.
[4] *Ibid.*, 1905, 159.
[5] *Ber.*, 1908, 41, 80.

dried at 110° C. till constant. The following values were obtained :—

	Total Precipitate in Grammes.	Insol. Aq. Diphenylmethane Derivatives.	Sol. Aq. Oxy-aminecarboxylic Acid.
		Per Cent.	Per Cent.
Phloroglucinol - -	2.4002	100	...
Hydroquinone - -	2.3716	100	...
,, - -	2.0542	100	...
Pyrogallol - - -	2.5150	100	...
,, - - -	2.7940	100	...
Pyrocatechol - -	2.9805	100	...
,, - -	2.9574	100	...
Resorcinol - -	2.9954	100	...
,, - - -	2.9725	100	...
Gallic acid - - -	2.0706	78.84	21.16
,, - - -	1.2240	83.18	16.82
,, - - -	1.1405	59.94	41.06
β-Resorcylic acid -	2.1040	51.08	48.92
,, ,, -	2.2008	47.12	52.88
Protocatechuic acid ·	...	...	...
,, ,, ˝	...	...	...
Vanillic acid - -	...	...	...
Tannin - - -	2.0599	...	Nearly all sol.
Digallic acid - -	2.1042	80.16	19.84
Leucodigallic acid -	2.0041	1.94	98.06

With the introduction of the carboxylic group the tendency of condensation to diphenylmethane derivatives is lessened ; by protocatechuic acid the tendency is *nil.* Nierenstein considers this reaction analogous to the formation of cork, to the genetic relation of which with the diphenylmethane formation Drabble and Nierenstein have referred in an earlier publication.[1] It is hence possible that the plants may employ formaldehyde as a methylation medium, and produce these insoluble condensation products for the purpose of ridding themselves of the poisonous phenols and aromatic hydroxy acids (and tannins), in addition to oxidising processes whereby phlobaphenes, ellagic acid, etc., are formed.

[1] *Biochemical Jour.*, 1907, 2, 96.

The reaction between phenols and aldehydes has been further studied by Michael,[1] who prepared a condensation product from phenol and resorcinol with benzaldehyde, and Russanow,[2] who also employed benzaldehyde and phenol. Lipp[3] investigated the action of benzaldehyde and piperonal on phenols, anisoles, cresols, cresylic ether, resorcinol, and the ether of the latter and phenol, and showed that when free phenols are condensed with benzaldehyde the hydroxyls occupy the same position as by the interaction between benzaldehyde and the corresponding phenolic ethers. The resulting dihydroxytriphenylmethane derivatives form beautiful crystals, which on oxidation are converted into benzaurines, the constitution of the latter probably being—
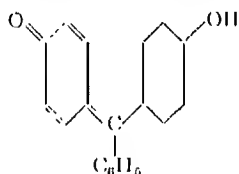
In alkalies, the hydroxylated triphenylmethanes dissolve without imparting any colour to the solution; by concentrated sulphuric acid they are taken up with intense coloration.

If the hydroxyls occupy the ortho-position to methyl, they may form xanthenes by splitting off water—
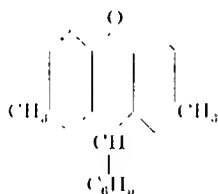
In the benzene series this reaction is difficult to establish, and has to be induced by distilling the particular dihydroxydiphenylmethane at ordinary pressure. In the naphthalene series, on the other hand, the ring closes up by, for instance,

[1] *Amer. Jour.*, 5, 338; 9, 130.
[2] *Ber.*, 1889, 22, 1944.
[3] Diss., Bern., 1905.

the condensation of β-naphthol with benzaldehyde or par-aldehyde, and yields the following compounds :—

$$C_6H_5-CH\begin{array}{c} C_{10}H_6 \\ \diagdown \\ C_{10}H_6 \end{array}\!\!>O \qquad CH_3-CH\begin{array}{c} C_{10}H_6 \\ \diagdown \\ C_{10}H_6 \end{array}\!\!>O$$

These xanthenes are white, silk-glossy needles, which are soluble in water and in alkalies. In concentrated sulphuric acid, they are taken up with beautiful fluorescence.

6. Summary

From the qualitative reactions of the different condensation products described it may be seen that their tannoid properties are not dependent on whether they precipitate gelatine or are adsorbed by hide powder or not. Hydroxy-naphthylmethanesulphonic acid, for instance, precipitates gelatine but does convert pelt into leather; on the other hand, sodium dicresylmethanesulphonate does not precipitate gelatine, and neither does it tan pelt; nevertheless it is adsorbed by hide powder as "tanning matter." The author discovered that o-nitrophenol does not precipitate gelatine, but has some tanning action on both hide powder and pelt.

Relatively to the possibilities of forming condensation products possessing tannoid properties, the following may be stated :—

All mono- and polyhydric phenols may be converted into true tanning matters by either condensing them as such, or after their conversion into the corresponding sulphonic acids, by substances capable of eliminating the elements of water. It makes no difference to the final product whether the condensation is the first step followed by sulphonation and consequent solubilisation of the intermediary insoluble product, or whether, vice versa, the sulphonic acid is subjected to condensation. Alkaline solution of phenols may also be condensed, the reaction products, when condensed, constituting tanning matters soluble in water.

Among the substitution products of the phenols, the thio-, chloro-, bromo-, nitro-, and aminophenols as a rule yield tanning matters similar in character.

The quinones are as such—*i.e.*, without being condensed—substances possessing tannoid properties.

The aromatic dihydric alcohols are easily condensed with the different sulphonic acids and yield valuable tanning matters.

Of aromatic acids all those which yield water-soluble sulphonation products seem suitable for the industrial production of tanning matters. If the acids themselves do not yield water-soluble sulphonation products, the alkali salts of the latter may be condensed with formaldehyde, and the resulting products then constitute tanning matters provided their solutions can be neutralised or faintly acidified without the solute being thrown out of solution in insoluble form.

The diphenyl derivatives of the above groups often possess tannoid properties.

The same holds good of those compounds with condensed nuclei (naphthalene, anthracene, etc.), and all their derivatives which satisfy the above conditions.

The choice of condensing agent is, as a rule, of little significance. Elimination of the elements of water by the mere application of heat succeeds in few cases only, since the high temperature required to induce reaction in many cases causes decomposition of the substances. This difficulty is overcome by heating *in vacuo*. Condensation with formaldehyde always succeeds, with acetaldehyde and benzaldehyde only partly.

The action on hide powder, pelt, and gelatine by these characteristic substances is tabulated below :—

Substance.	Relative Behaviour towards		
	Gelatine.	Hide Powder.	Pelt.
Formaldehyde - - - -	...	...	Tanning
Phenol - - - -	Ppte.	...	...
Chlorophenol - - - -	,,	...	...
Tribromophenol [1] - - -	Slight ppte.	Tanning	Surface tanning
o-Nitrophenol - - - -	No ppte.	,,	,,
Bromonitrophenol - - -	Slight ppte.	,,	,,
Trinitrophenol - - -	Ppte.	,,	Tanning
Bromotrinitrophenol - - -	Slight ppte.	,,	,,
p-Aminophenol - - -	Ppte.	...	...
m-Dihydroxybenzene - - -	,,	...	...
Orcinol - - - -	,,	...	...
p-Dihydroxybenzene - - -	,,	Tanning	Tanning
Monochloro-p-dihydroxybenzene	,,	...	...
o-Dihydroxybenzene - -	,,	...	...
Pyrogallic acid - - -	,,	...	...
Tribromopyrogallic acid - -	,,	Tanning	Surface tanning
Gallic acid - - - -	No ppte.	Not tanning	Not tanning
Bromophloroglucinol - - -	Ppte.	Tanning	,,
Gallotannic acid - - -	,,	,,	Tanning
Galloflavine - - - -	Slight ppte.	,,	Not tanning
Quinone - - - -	,,	,,	Tanning
Bromosalicylic acid - -	,,	,,	Not tanning
Dinaphthylmethanedisulphonic acid	Ppte.	,,	Tanning
Diphenylmethanedisulphonic acid	,,	,,	,,
Dicresylmethanedisulphonic acid	,,	,,	,,
Sodium dicresylmethanedisulphonate	No ppte.	,,	Not tanning
Dixylylmethanedisulphonic acid -	Ppte.	,,	Tanning
Naphtholdisulphonic acid - -	,,	Not tanning	Not tanning
Methylenedinaphthol - - -	,,	Tanning	Tanning
Hydroxyphenylmethanesulphonic acid	...	...	Not tanning
Hydroxynaphthylmethanesulphonic acid	Slight ppte.	...	,,
Diaminonaphthylmethanedisulphonic acid	Ppte.	Tanning	Tanning
Dihydroxynaphthylmethanedisulphonic acid	,,	,,	,,
Dichloronaphthylmethanedisulphonic acid	,,	,,	Surface tanning
Dinitronaphthylmethanedisulphonic acid	,,	,,	,,
Dithionaphthylmethanedisulphonic acid	,,	,,	Tanning
Bromo-β-naphthol [1] - - -	Slight ppte.	,,	,,
Rosolic acid [1] - - - -	Ppte.	,,	,,

[1] In alcoholic solution.

SECTION III

TANNING EFFECTS OF MIXTURES AND NATURAL PRODUCTS

1. Mixture of Phenolsulphonic Acid and Formaldehyde

THE most important invention relatively to the search for new tanning materials was that of Weinschenk,[1] who first showed that pelt may be converted into leather by the action upon it of mixtures of naphthols and formaldehyde. This process consists of two steps : the pelt is first immersed in a 0.25-0.50 per cent. formaldehyde solution, and secondly in an aqueous solution of α- or β-naphthol ; this order may be reversed. If, on the other hand, a pasty mixture is made of formaldehyde and naphthol, and this is allowed to act upon the pelt, the latter is rapidly converted into leather, but the mixture must be administered very gradually or otherwise the insoluble methylenedinaphthol is formed outside the pelt and hinders any tanning effect.

Leather obtained through the action of α-naphthol is, when freshly tanned, pure white and sufficiently soft and firm, but quickly assumes a brown colour on storing ; if, however, β-naphthol is employed, a cream-coloured leather results, the colour of which turns only slightly more yellowish even when exposed to the direct rays of the sun.

A similar process has recently (25, xii., 1915) been protected by Ger. Pat., 305,516, granted to the Deutsch-Koloniale Gerb- und Farbstoff Gesellschaft, in Karlsruhe. According to this patent, pelt is treated in separate solutions, one of which is formaldehyde, the other being that of such aromatic compounds or their salts which yield water-soluble condensation products with formaldehyde ; for example, pelt is immersed in 2-5 per cent. solution of formaldehyde for a few days, and is subsequently treated with 1-2 per cent.

[1] Ger. Pat., 184,449.

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neutral or faintly acidified solutions of α-naphthylamine hydrochloride, resorcinol or sodium phenate or cresylate, for several days. The resultant leather is claimed to be soft and full and to possess good tensile strength.

The tanning properties of mixtures of phenolsulphonic acid and formaldehyde have been examined by the author with the following results :—

	I.	II.	III.
Grammes formaldehyde - - -	10	20	40
" phenolsulphonic acid - -	20	50	100
" caustic soda (sol., 40 per cent.)	10	20	40
" water - - - - -	500	500	500

The above solutions were made up and allowed to act upon pelt pieces weighing 15 gm.; whereas Solution I. remained clear throughout the experiment, Solution II. became somewhat clouded, and Solution III. assumed a milky appearance. The pelts were tanned through in seven days and yielded leathers which, after drying and finishing, possessed yellow colour, long fibre, and good tensile strength, but a rather empty feel.

To prevent separation of insoluble matter during tannage, another experiment was carried out, in which the pelts were first submitted to the action of formaldehyde (10, 20, and 40 gm. in 500 c.c. water) for three days, being subsequently removed to fresh solutions of partly neutralised phenol-sulphonic acid (cf. above). Similar results were obtained, but the leather felt even more empty than those obtained by the former experiment.

Attempts at converting pelt into leather by first immersing the pelt in a partly neutralised solution of phenolsulphonic acid, and subsequently transferring it to fresh solutions of formaldehyde, gave merely negative results ; the phenol-sulphonic acid effected pickling action upon the pelt, but was subsequently quickly replaced by the formaldehyde, before the latter had penetrated the pelt in sufficient quantity to induce condensation, thereby exerting tanning action.

To explain the tanning effects of these mixtures, the author analysed the leathers resulting from the effects of the latter, and was able to show, that in these cases also, condensation of phenolsulphonic acid and formaldehyde takes place *inside* the pelt, since on the one hand the analyses left no doubt but that true tannage had been effected, and on the other hand an ammoniacal extract of the leathers gave the typical reaction for condensation products of phenolsulphonic acid, with aniline hydrochloride.[1]

The leather analyses gave the following figures :—

Moisture	-	-	-	18.30 per cent.
Fats -	-	. -	-	0.47 ,,
Ash -	-	-	-	0.98 ,,
Leather ⎰Tannin	-	-	-	26.37 ,,
substance ⎱Hide substance	-	-	-	53.88 ,,

A characteristic feature is the low value of tannin, which is considerably higher[2] where condensation products of phenolsulphonic acids are used as tanning agents; the action effected by the separate constituents, therefore, is more that of pickling.

2. Mixture of Phenolsulphonic Acid and Natural Tannins

A piece of pelt was immersed in a half-neutralised solution, measuring 6° Bé., of phenolsulphonic acid, and left sixteen hours in the solution, which completely penetrated the pelt during this time; it was then transferred to a 12° Bé. solution of a mixture of quebracho and chestnut, which in two days converted the pelt into a light coloured leather possessing good tensile strength.

By using a bath composed of half-neutralised phenol-sulphonic acid and quebracho extract in 7° Bé. solution, another piece of pelt was completely tanned in two days. The same result was obtained by first half neutralising the phenolsulphonic acid and then adding sulphited quebracho extract till a 5° Bé. solution was obtained.

[1] *Collegium*, 1913, 516, 142.
[2] *Ibid.*, 1913, 521, 478.

A piece of pelt received a 2° Bé. liquor composed of 3 parts of phenolsulphonic acid and 1 part of formaldehyde for sixteen hours, and was then completely penetrated; it was subsequently transferred to a 10" Bé. liquor composed of chestnut and quebracho, being completely tanned in two days. The same result was obtained on adding sufficient sodium sulphate to the above mixture of phenolsulphonic acid and formaldehyde to raise the density from 2"-3" Bé.

Sixty grammes of phenolsulphonic acid were partly neutral-ised with 100 c.c. of a 10 per cent. solution of caustic soda, and 10 c.c. formaldehyde added to 400 c.c. of the mixture (2" Bé.): a piece of pelt was completely penetrated by the solution in sixteen hours, and was subsequently tanned in two days, using an extract of 10" Bé. Similarly, by treating a pelt with 400 c.c. of a half-neutralised solution of phenolsulphonic acid (3° Bé.) plus 8 c.c. formaldehyde, and adding after eighteen hours sulphited quebracho extract to the same bath, strengthening the latter to 6" Bé., the pelt was converted into leather in two days; in this case, however, much of the tannin was precipitated by the formaldehyde present in the solution. If, on the other hand, a mixture of 80 gm. dilute phenolsulphonic acid (1 : 1 aq.) and 14 gm. of for-maldehyde were cooled for several hours and subsequently strengthened with sulphited quebracho extract to 7" Bé., no tannin was precipitated in the liquor, and a piece of pelt immersed in the latter was completely tanned in sixteen hours.

To prevent the precipitation of tannin caused by the formaldehyde, sulphite cellulose extract (wood pulp) was substituted for sulphited quebracho extract, and the following experiments carried out :—

To 200 c.c. of a 6" Bé. sulphite cellulose extract plus 200 c.c. of half-neutralised phenolsulphonic acid solution was added 15 c.c. formaldehyde, and this solution tanned pelt in four days; the resultant leather was light brown, firm, and possessed good tensile strength and long fibre.

Another piece of pelt was immersed in a solution of 400 c.c. phenolsulphonic acid of 3" Bé. plus 15 c.c. formalde-hyde for eighteen hours, and was then tanned in a 6" Bé.

solution of sulphite cellulose extract. The resultant leather was extremely light coloured, and possessed qualities similar to those described in the former experiment. Finally, pelt was immersed in a 6° Bé. solution composed of 140 gm. of a 15° Bé. sulphite cellulose extract, 10 gm. of formaldehyde, 400 gm. water, 15 gm. phenolsulphonic acid, and 30 gm. of a 10 per cent. caustic soda solution, and was tanned in four days. This leather also was coloured light brown, of good tensile strength, and rather firm.

These experiments prove that when pelt is treated with formaldehyde, phenolsulphonic acid, and vegetable tannins, the two former components effect, more or less, actual tannage; it is admittedly a matter of some difficulty to establish whether the effect is one of pickling or pseudo-tannage, or whether the tannage may be considered a true one. The final effect, however, is nearly always that of a true tannage, *i.e.*, by varying the composition of the tanning solutions leather is obtained with properties identical with those tanned with true tannins of vegetable origin. The only difficulty encountered in these combinations is the property of formaldehyde, of precipitating the natural tannins, and it is hence essential, for practical purposes, to so arrange the combination that their value is not reduced by the property referred to. The fact that not only compounds already existing may convert pelt into leather, but that a similar effect is obtained *inside the pelt*, by their components, is indeed of theoretical interest.

3. Tanning Effects of Different Natural Substances

In addition to the vegetable tannins, Nature has also provided other substances of vegetable origin, which, admittedly, do not effect tannage in their original state, but which may, by suitable treatment, acquire this property. The oldest information on this point is supplied by Resch,[1] who carried out tanning experiments, using three parts of peat and one part of oak bark.

By the action of nitric acid on substances of vegetable

[1] *Scherer's Jour.*, 1801, 6, 495.

and animal origin, Hatchett,[1] Chevreul,[2] and Vogel[3] claim to have obtained tanning materials, whilst later, Buff[4] obtained a material suitable for tanning purposes from indigo.

By subsequent treatment with lime and soot, or tar, Ashmore[5] claims to have converted pelt into leather.

By treating peat with nitric acid, Jennings[6] and Payne[7] have produced artificial tanning materials.

Skey[8] obtained a dark brown extract, soluble in water and precipitating gelatine, by treating bituminous coal or lignite with nitric acid; by extracting coal with alkalies, Reinsch[9] isolated a substance (pyrofuscine) which, when partly neutralised with carbon dioxide, was capable of converting pelt into leather.

In addition to these tanning materials the recovery of a substance possessing tanning properties from the so-called acid rosins has been made the subject of a patent;[10] this rosin is formed when crude oil is treated with concentrated sulphuric acid in the oil refineries. The greasy substance is partly neutralised with alkali and is claimed to produce a very springy leather.

The waste liquors obtained in the manufacture of cellulose, the so-called sulphite and sodium cellulose waste, have, however, been the subject of numerous investigations, and several hundred publications have appeared and a great number of patents[11] taken out, the first one being that of Mitscherlich[12] and Hönig.[13]

The waste liquors contain large quantities of acids and

[1] *Gehlen's Jour.*, 1805, 1, 545.

[2] *Ann. Chim.*, 1810, 73, 36.

[3] *Jour. Chem. Phys.*, 1812, 6, 101.

[4] *Ibid.*, 1827, 51, 38.

[5] *Dingler's Jour.*, 1833, 48, 67.

[6] *Jahresber. d. Chem.*, 1858, 666.

[7] *Chem. Centralbl.*, 1908, ii. 554; Ger. Pat., 200,539.

[8] *Chem. News*, 1866, 206; *Zeits. f. Chem.*, 1866, 753.

[9] *Pharm. Centralh.*, 1887, 141.

[10] Ger. Pat., 36,019.

[11] "Literatur über Sulfitablauge," 1910-13. (Reprint from *Wochenbl. f. Papierfabrikation.*)

[12] *Jahresber. d. Chem.*, 1893, 890; Ger. Pat, 72,161.

[13] *Chem. Centralbl.*, 1902, ii. 174; Ger. Pat., 132,224.

lime, and in order to utilise the liquors for tanning purposes, the excessive sulphuric and sulphurous acids as well as the lime must be removed. The active tannin is no doubt the ligninsulphonic acid, and those cellulose extracts containing the largest amounts of free ligninsulphonic acid may also be considered the most efficient.

According to the author,[1] such sulphitecellulose extracts precipitate gelatine, aniline hydrochloride, ammoniacal zinc acetate, and basic coal-tar dyes, and give a greenish-black coloration with ferric chloride. These reactions indicate the presence of tanning matters in cellulose extracts.

The official shake method of analysis gives the following results :—[2]

Tanning matters	-	-	-	23.0 per cent.	
Non-tannins -	-	-	-	30.3	,,
Insoluble matters	-	-	-	0.7	,,
Water	-	-	·	46.0	,,
				100.0 per cent.	
Ash -	-	-	-	4.3	,,
Sulphurous acid	-	-	-	0.6	,,

Many other substances have been used for tanning experiments, a number of them precipitating gelatine. Zacharias[3] obtained leather by the action of many coal-tar dyes on pelt, similarly Herzog and Adler, by using Prussian blue, Neufuchsin, patent blue V, crystal violet, and colloidal gold.

Most inorganic substances possess tanning properties when in the colloidal state, e.g., sulphur, halogens, chromium salts, iron salts, silver oxide, and the salts of mercury, copper, bismuth, zinc, lead, platinum, cesium, vanadium, and the rare earths (salts of cerium, lanthanum, didymium, neodymium, thorium, and zerconium).

For practical purposes, however, only sulphur, chrome, and alum salts are used, the latter two being of the greatest importance.

[1] *Technikum*, 1912, 20, 156.
[2] *Ibid.*
[3] *Zeits. f. Ang. Chem.*, 1907, 1645.

SECTION IV

METHODS OF EXAMINING TANNING MATTERS

WHEREAS the evaluation of vegetable tanning matters necessitates determinations of their practical applicability in addition to qualitative and quantitative analyses, the latter two determinations are of practically no value when dealing with synthetic tannins. The way in which tanning matters obtained by chemical means exert their action, in addition to the intensity with which they convert pelt into leather, is the only criterion of their quality for practical (tanning) purposes ; both may be demonstrated by experimental tests.

When dealing with the natural tanning materials it is desirable to know their contents of actual tanning matter, from which their special qualities as tanning agents may be deduced. Where the vegetable tanning materials have already been converted into extracts, it is essential to establish the identity of the original material used by the qualitative reactions of the extract in addition to the quantitative estimation of actual tannin contents. It is frequently necessary to examine whether the extract in question has been actually prepared from the material giving the extract its name, or whether the extract has suffered the addition of other extracts of tanning materials of but low quality. Such determinations may be undertaken by microscopical observations and by means of qualitative and quantitative reactions ; for this purpose many colour reactions and precipitation methods are available in addition to the determination of the molybdenum figure (Lauffmann),[1] the alcohol and ethyl acetate figures and microscopical examination (Grasser).[2] Of other adulterants tending to reduce the quality of extracts may be

[1] *Collegium*, 1913, 10.
[2] *Ibid.*, 1911, 349.

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of the method. The latest instructions, which are reprinted below, permit of any method of analysis which observes the following conditions :—

1. The solution for analysis must contain between 3.5 and 4.5 gm. of tanning matter per litre, and solid materials must be extracted so that the greater part of the tannin is removed at a temperature not exceeding 50° C.

2. The total solubles must be determined by the evaporation of a measured quantity of the solution previously filtered till optically clear, both by reflected and transmitted light. This is obtained when a bright object such as an electric light filament is distinctly visible through at least 5 cm. thickness, and a layer of 1 cm. deep in a beaker placed on a black glass or black glazed paper appears dark and free from opalescence when viewed from above. Any necessary mode of filtration may be employed, but if such filtration causes appreciable loss when applied to a clear solution, a correction must be determined and applied as described in paragraph 6.

Filtration shall take place between the temperatures of 15° C. and 20° C. Evaporation to dryness shall take place between 98.5° C. and 100° C. in shallow, flat-bottomed basins, which shall afterwards be dried until constant at the same temperature, and cooled before weighing for not less than twenty minutes in air-tight desiccators over dry calcium chloride.

3. The total solids must be determined by drying a weighed portion of the material, or a measured portion of its uniform turbid solution, at a temperature between 98.5° C. and 100° C. in shallow, flat-bottomed basins, which shall afterwards be dried until constant weight at the same temperature, and cooled before weighing for not less than twenty minutes in air-tight desiccators over dry calcium chloride.

"Moisture" is the difference between 100 and the percentage of total solids, and "insoluble" the difference between "total solids" and "total solubles."

4. *Non-Tannins.*—The solution must be detannised by shaking with chromed hide powder till no turbidity or

opalescence can be produced in the clear solution by salt-gelatine solution. The chromed powder must be added in one quantity equal to 6.0-6.5 gm. of dry hide powder per 100 c.c. of the tanning solution, and must contain not less than 0.2 per cent. and not more than 1 per cent. of chromium calculated on the dry weight, and must be so washed that in a blank experiment with distilled water, not more than 5 mg. of solid residue shall be left on evaporation of 100 c.c. All water contained in the powder should be determined and allowed for as water of dilution.

5. *Preparation of Infusion.*—Such a quantity of material shall be employed as to give a solution containing as nearly as possible 4 gm. of tanning matter per litre, and not less than 3.5 or more than 4.5 gm. Liquid extracts shall be weighed in a basin or beaker and washed with boiling water into a litre flask, filled up to the mark with boiling water, and well mixed and rapidly cooled to a temperature of 17.5″ C., after which it shall be accurately made up to the mark, again well mixed, and filtration at once proceeded with. Sumac and myrabolam extracts should be dissolved at a lower temperature.

Solid extracts shall be dissolved by stirring in a beaker with successive quantities of boiling water, the dissolved portions being poured into a litre flask, and the undissolved being allowed to settle and treated with further portions of boiling water. After the whole of the soluble matter is dissolved, the solution is treated similarly to that of a liquid extract.

Solid tanning materials, previously ground till they will pass through a sieve of sixteen meshes per square centimetre, are extracted in Koch's or Procter's extractor with 500 c.c. of water at a temperature not exceeding 50″ C.; the extraction is then continued with boiling water till the filtrate amounts to 1 litre. It is desirable to allow the material to soak for some hours before commencing the percolation, which should occupy not less than three hours, so as to extract the maximum of tannin. Any remaining solubles in the material must be neglected or reported separately as "difficultly soluble" substances.

The volume of liquid in the flask must, after cooling, be accurately made up to 1 litre.

6. *Filtration.*—The infusion shall be filtered till optically clear (*vide* 2). No correction for absorption is needed for the Berkefeld candle, or for S. and S. 590 paper [1] if a sufficient quantity (250-300 c.c.) is rejected before measuring the quantity for evaporation, and the solution may be passed through repeatedly to obtain a clear filtrate.

If other methods of filtration are employed, the average correction necessary must be determined in the following manner:—About 500 c.c. of the same or a similar tanning solution is filtered perfectly clear, and after thorough mixing 50 c.c. is evaporated to determine " Total Soluble A." A further portion is now filtered in the exact method for which the correction is required (time of contact and volume rejected being kept as constant as possible), and 50 c.c. is evaporated to determine " Total Soluble B." The difference between " A " and " B " is the correction sought, which must be added to the weight of the total solubles found in analysis. An alternative method of determining correction, which is equally accurate and often more convenient, is to filter a portion of the tanning solution through the Berkefeld candle till optically clear, which can be generally accomplished by rejecting 300 or 400 c.c., and returning the remaining filtrate repeatedly; and at the same time to evaporate 50 c.c. of the clear filtrate obtained by the method for which correction is required, when the difference between the residues will be the correction sought. An average correction must be obtained from at least five determinations. It will be found that this is approximately constant for all materials, and amounts in the case of S. and S. 605, 150 c.c. being rejected, to about 0.005 gm., and where 2 gm. of kaolin are employed in addition to 0.0075 gm. The kaolin must be previously washed with 75 c.c. of the same liquor, which is allowed to stand fifteen minutes and then poured off. Paper 605 has a special absorption for a yellow colouring matter often contained in sulphited extracts.

[1] Schleicher and Schull, Duren (Rheinland), Germany.

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7. Hide powder shall be of a woolly texture, thoroughly delimed, preferably with hydrochloric acid. It shall not require more than 5 c.c. or less than 2.5 c.c. of decinormal NaOH or KOH to produce a permanent pink colour with phenolphthalein on 6.5 gm. of the dry powder suspended in water. If the acidity does not fall within these limits it must be corrected by soaking the powder before chroming for twenty minutes in ten to twelve times its weight of water, to which the requisite calculated quantity of standard alkali or acid has been added. The hide powder must not swell in chroming to such an extent as to render difficult the necessary squeezing to 70-75 per cent. of water, and must be sufficiently free from soluble organic matter to render it possible in the ordinary washing to reduce the total solubles in a blank experiment with distilled water below 0.005 gm. per 100 c.c. The powder, when sent out from the maker, shall not contain more than 12 per cent. of moisture, and shall be sent out in air-tight tins.

The detannisation shall be carried out in the following manner :—

The moisture in the air-dried powder is determined, and the quantity equal to 6.5 gm. actual dry powder is calculated, which will be practically constant if the powder be kept in an air-tight vessel. Any multiple of this quantity is taken according to the number of analyses to be made, and wet back with approximately ten times its weight of distilled water. Two grammes per 100 of dry powder of crystallised chromic chloride, $CrCl_3.6aq.$, is now dissolved in water and made basic with 0.6 gm. of Na_2CO_3 by the gradual addition of 11.25 c.c. of normal Na_2CO_3, thus making the salt correspond to the formula $Cr_2Cl_4(OH)_2$. In laboratories where analyses are continually being made, it is more convenient to employ a 10 per cent. stock solution, made by dissolving 100 gm. of $Cr_2Cl_6.6aq.$ in a little distilled water in a litre flask and very slowly adding a solution containing 30 gm. of anhydrous sodium carbonate, with constant stirring, finally making up to the mark with distilled water and well mixing. Of this solution 20 c.c. per 100 gm., or 1.3 c.c. per 6.5 gm. of dry powder, should be used. This solution is added to the

powder, and the whole churned for one hour. At the end
of the one hour the powder is squeezed in linen to free it
as far as possible from the residual liquor, and washed and
squeezed repeatedly with distilled water, until, on adding to
50 e.e. of the filtrate one drop of 10 per cent. K_2CrO_4 and
four drops of decinormal silver nitrate, a brick-red colour
appears.   Four or five squeezings are usually sufficient.
Such a filtrate cannot contain more than 0.001 gm. of NaCl
in 50 c.c.

The powder is then squeezed to contain 70-75 per cent.
of water, and the whole weighed.   The quantity Q containing
6.5 gm. dry hide is thus found, weighed out, and added
immediately to 100 c.c. of the unfiltered tannin infusion along
with (26.5-Q) of distilled water.   The whole is corked up and
agitated for fifteen minutes in a rotating bottle at not less
than 60 revs. per minute.   It is then squeezed through linen,
the fitrate stirred and filtered through a folded filter of
sufficient size to hold the entire filtrate, returning till clear.
Sixty c.c. of the filtrate is then evaporated and calculated as
50 c.c., or the residue of 50 e.c. multiplied by 6/5.   The
non-tannin filtrate must give no turbidity with a drop of a
solution of 1 per cent. gelatine and 10 per cent. common salt.[1]

One gramme of kaolin, freed from all soluble matter, may
be added to the filtrate, or it may be used by mixing it with
the hide powder in the shaking bottle.

The analysis of used liquors and spent tans shall be made
by the same methods as are employed for fresh tanning
materials ; the liquors being diluted, are concentrated by
boiling *in vacuo,* or in a vessel so closed as to restrict access
of air, until the tanning matter is if possible between 3.5 and
4.5 gm. per litre, but in no case beyond a concentration of
10 gm. per litre of total solids, and the weight of hide powder
used shall not be varied from 6.5 gm.

The results shall be reported as shown by the direct
estimation, but it is desirable that in addition efforts shall
be made, by determination of acids in the original solution

[1] It is convenient for technical purposes to employ the commercially
obtainable chromed hide powder as prepared, for instance, by the
German Experimental Station at Freiberg, Saxony.

and in the non-tannin residue, to ascertain the amount of lactic and other non-volatile acids absorbed by the hide powder, and hence returned as "tanning matters."

In the case of tanning materials it must be clearly stated in the report whether the calculation is on the sample with moisture as received, or upon some arbitrarily assumed percentage of water; and in that of liquors whether the percentage given refers to weight or to grammes per 100 c.c., and in both cases the specific gravity shall be reported.

All analyses reported must be the average result of duplicate determinations, which must agree in the case of liquid extracts within 0.6 per cent., and of solid extracts within 1.5 per cent., or the analysis shall be repeated until such agreement is obtained.

All reports shall be marked : Analysed in accordance with the rules of the S.L.T.C. (I.A.L.T.C.)—when the analyses have been carried out according to the method described above.

As has been repeatedly emphasised in this treatise, the synthetic tannins form a special class of substances, and the results obtained by either of the two hide-powder methods do not give figures which are always comparable to those of the natural tannins. An example of the inapplicability of the methods where synthetic tannins are concerned is illustrated by the behaviour towards hide powder of them when partly neutralised to varying degrees: commercial Neradol D of acidity 1 gm. = 10 c.c. N/10 NaOH contains 33 per cent. tanning matters, completely neutralised Neradol D, which exerts no true tanning action on pelt, still contains 20 per cent. tanning matter when analysed according to the Official Method ; a difference hence exists regarding the adsorption by hide powder of a tannin and the adsorption of the latter by hide. As, however, we are unable to make a distinction between these two different properties by using hide powder only, we are also unable to draw the factor into account.

Another source of error is the swelling influence on hide powder by acids ; for instance, an acid extract of vegetable tannins would show higher tannin contents in the analysis than would the same extract when less acid. The free sulphonic acid, however, is the active principle in synthetic

tannins, and since the latter always contain other acids (of organic and inorganic origin) devoid of tannoid character, a source of error is thus introduced, which we cannot eliminate by the present method of analysis.

Of other methods of estimating the quality of a tanning material or tanning extract the *determination of solubility, ash, colour,* and *weight-giving properties* in addition to the *firmness imparted to the leather* by the particular material are of importance. As regards the synthetic tannins they are as a rule very soluble and it will generally be found sufficient to subject them to the ordinary qualitative examination. The ash determination in synthetic tannins, on the other hand, is not of such value as in the case of natural tanning extracts. From their composition we know that synthetic tannins contain considerable quantities of mineral salts, the presence of some of which on the one hand emphasises their pickling effect, and that on the other hand the property of dissolving phlobaphenes exhibited by the synthetic tannins is closely connected with their salt contents.

A colour determination of synthetic tannins is not of much importance, since synthetic tannins nearly always impart a white or light brown colour to the hide. In those cases only where coloured decomposition products appear as a result of intermediary reactions, may the former impart greyish or dirty colorations of little beauty to the hide. This is easily ascertained by lightly tanning a pelt.

The determination of the weight and solidity-giving properties is important both for leathers tanned with vegetable tanning extracts and for those treated with synthetic tannins, but the results obtained when using animalised cotton are not directly convertible into figures required for practical purposes. Comparative figures are better obtained by actually tanning pieces of pelt on as practical a scale as is possible, and testing the weights and tensile strengths of the pieces as against those of the original pelts, whereby in the former case the yield (pelt——→leather) is obtained.

Its capability as a tanning agent may be ascertained by submitting the synthetic tannin to an actual test tannage. The latter is carried out by introducing the dilute extract

into open glass jars, holding about 400 c.c. at a width of about 8 cm.[1] The concentration of the solution is chosen according to acidity and salt contents of the synthetic tannin, the most suitable being 1.5°-2.5° Bé. A piece of bated pelt is suspended in the liquor in such a way that the pelt is completely surrounded by liquor, without, however, being creased or touching the bottom. If the pelt were creased during tannage, the wrinkles would become fixed and would show in the finished leather. Thus an unfair judgment of the extract would be delivered, since similar results are produced by liquors which are either too concentrated or are not properly composed, and naturally this property of an extract would be greatly to its disadvantage.

The various stages of tannage may be judged from various standpoints when examining the pelt as tannage proceeds. On the one hand, the surface of the but slightly porous pelt is altered so as to present a more porous appearance, which is now rendered more capable of absorbing liquids. On the other hand, a similar alteration takes place *within* the pelt, to the extent to which the tanning matter has penetrated it. How far the penetration has proceeded is easily determined by utilising the different adsorption of coal-tar dyes by untanned and tanned pelt (see p. 121). An indicator for those synthetic tannins, which are derived from the phenols, is ferric chloride, which only colours those parts of the pelt which have been penetrated by the synthetic tannins ; clearer and better results are, however, obtained when the dyestuffs referred to above are employed.

As soon as the tanning matter has completely penetrated the pelt, the total time of tannage is noted, and the velocity with which the tanning matter converts the pelt into leather at that particular concentration is thus obtained. The tannage completed, the leather must be well washed in running water to remove excess of synthetic tannin and then dried. On examining the dry leathers, the colour may then be observed, and a cut will give an idea of the tensile strength and the length of fibre of the leather. The tensile strength is, however, not of much value in such a barely tanned leather

[1] Accumulator jars are excellent for the purpose.— *Transl.*

and cannot be compared with that obtained in leathers tanned
on a practical scale.   The length of fibre is, however, of some
importance, since a special feature of finished leathers tanned
with synthetic tannins is the beautifully long fibre—a property
which manifests itself when the leather is torn and in which
an expression of the quality of the synthetic tannin may be
found.

Similarly, tanning experiments combining synthetic and
natural tannins may be carried out, the most interesting
features of these being the different proportions in which the
two products are mixed.   Such experiments may be done, for
instance, by preparing $2°$ Bé. solutions of each extract and
then mixing them in proportions of, say, 10 : 90, 20 : 80, 30 : 70,
etc.   Here it is again possible to infer the *tanning intensity* of
the synthetic tannin from the concentration and the time used
for tannage.

A further determination of the quality of a synthetic
tannin is the capability of the latter of dissolving or pre-
cipitating the natural tannins.   As is well known, synthetic
tannins frequently possess the practically important property
of rendering natural tannins easily soluble in water.   In some
cases, however, synthetic tannins appear to solubilise natural
tannins in concentrated solutions ; when, however, the latter
are diluted, the natural tannin is precipitated with varying
completeness, the reason of which is often the presence of
excessive acid or the presence of such salts as have no
phlobaphene-solubilising properties.

For practical purposes this determination may be carried
out by mixing, in different proportions, concentrated tannin
solutions and the synthetic tannin ; heating the mixture on
the water bath for a short time, cooling and finally diluting
10, 20, and 30 gm. of the mixture to 100 c.c., which are then
left in measuring cylinders for twelve to twenty-four hours ;
the amount deposited will then be an indication of the
solubilising or precipitating effect exhibited by the synthetic
tannin.

Other properties of the synthetic tannins connected with
their practical application will be discussed in Part II. of this
treatise.

PART II
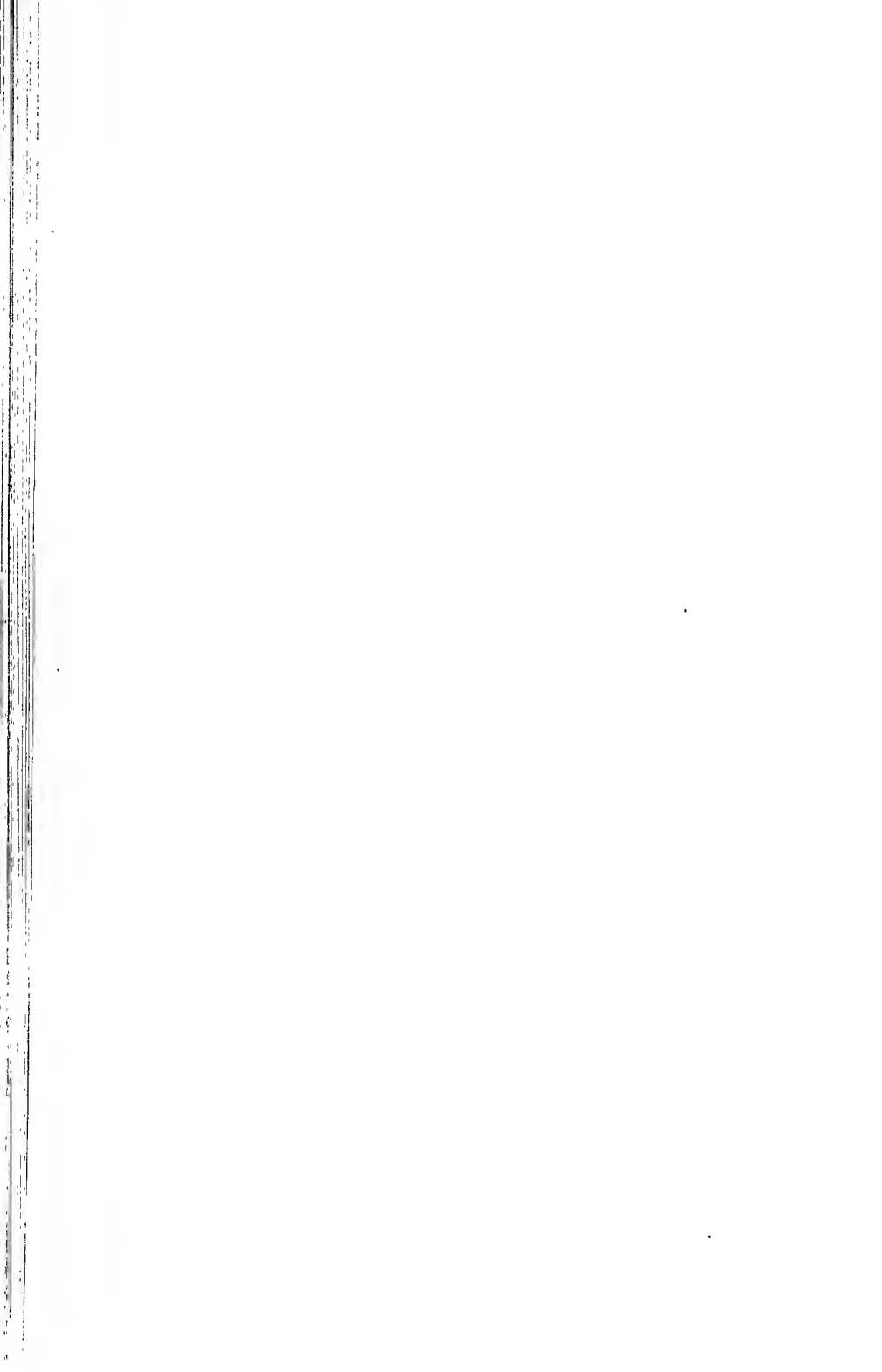
SYNTHETIC TANNINS: THEIR INDUSTRIAL
PRODUCTION AND APPLICATION

WITH regard to their *industrial production*, but few synthetic
tannins are, to-day, of practical and commercial interest.   In
addition to simplicity in the method of manufacture a certain
degree of purity of the raw materials constitutes the criterion
of their suitability.   The methods of manufacture, of which
nearly all are the property of the B.A.S.F., have been so
worked out that the production of synthetic tannins presents
no difficulties on a practical scale.   Cresols, naphthalenes, and
higher hydrocarbons are used as starting materials in the
production of synthetic tannins ; the former substances or
their oxidation products are sulphonated by means of con-
centrated sulphuric acid, and the tanning matter produced
by condensing the sulphonic acids with formaldehyde.   The
crude synthetic tannin thus obtained has yet to be diluted
and partly neutralised before it can be applied in practice,
and this is carried out by mixing the crude product with
strong caustic lye.   By these means the high acidity is
reduced to a suitable degree learned from experience on the
one hand ; on the other hand, the salts of the sulphonic
acids form valuable components of the commercial synthetic
tannins.

The first product placed on the market was named
Neradol D; this represents the condensation product of
cresolsulphonic acid.   The second synthetic tannin was
Neradol N, which represents the condensation product of
naphthalenesulphonic acid ; when diluted and neutralised to
the same extent as is done in the case of Neradol D, the
product is named *Neradol ND*.   The latest synthetic tannin
has been called *Ordoval G*, the starting material of which is
a still higher hydrocarbon.

The tannoid-chemical properties of these synthetic tannins
have been exhaustively determined by the author, who

employed Neradol D, which is most suitable for such a pur-
pose, and the investigations relating to it will now be treated
fully in the following chapters. The two other synthetic
tannins exhibit very similar properties, but their few charac-
teristics shall be shortly dealt with.

The condensation product obtained by the method de-
scribed on p. 55 forms a viscous, dark coloured mass, the
analysis of which by the shake method gives the following
figures :—

Tanning matters	-	-	-	62.6	per cent.
Non-tannins -	-	-	-	6.4	,,
Insolubles -	-	-	-	0.0	,,
Water -	-	-	-	31.0	,,

100.0 per cent.

Acidity : 1 gm. = 40 c.c. N/10 NaOH.

According to its chemical constitution, this product may
be considered to be dinaphthylmethanedisulphonic acid.

Samples of this crude, strongly acid material were partly
neutralised, and the following figures obtained on analysis :—

Acidity.				Tanning Matters.	Soluble Non-tans.	Water.
				Per Cent.	Per Cent.	Per Cent.
1 gm. = 35 c.c. N/10 NaOH	-	-		61.8	7.0	31.2
1 ,, = 30 ,, ,,	-	-		58.9	7.1	34.0
1 ,, = 25 ,, ,,	-	-		50.1	7.9	42.0
1 ,, = 20 ,, ,,	-	-		42.2	8.9	48.9
1 ,, = 15 ,, ,,	-	-		37.4	10.4	52.2
1 ,, = 10 ,, ,,	-	-		31.6	13.6	54.8
1 ,, = 5 ,, ,,	-	-		26.3	16.6	57.1

Experimental tanning tests which were carried out with
the various partly neutralised samples yielded leathers which,
on an average, were nearly white, but which in comparison
with a leather tanned with Neradol D appeared rather more
greyish and were much harder.

A solution of the half-neutralised substance (1 gm. = 20 c.c. $N/10$ NaOH) gives the following reactions:—

Gelatine - - -	- Precipitate, partly soluble in excess tannin solution.
Ferric chloride - -	- No coloration.
Barium chloride - -	- Precipitate, insoluble HNO_3.
Bromine water - -	- No reaction.
Silver nitrate - -	- No reaction.
Aniline hydrochloride -	- Precipitate, dissolves when solution is heated.

This condensation product is very soluble in water, but insoluble in most solvents, excepting methyl and ethyl alcohols. The above reactions show the similarity of this dinaphthyl derivative to 'the dicresyl derivative, and the absence in the former of characteristic reactions with iron salts is mainly accounted for by its lack of phenolic groups. The absence of this reaction does not, of course, influence the tannoid character of dinaphthylmethanedisulphonic acid in the least, and is of no importance in practice, since the various stages of tannage may be demonstrated by means of a solution of indigotine (see p. 121).

From a technical point of view the absence of this reaction is advantageous to this extent, that it eliminates the exceedingly great care to avoid the contact of tan liquors and tanned pelt with iron particles which has to be observed when tannins of phenolic character are employed.

In a chemical and technological evaluation of this tanning matter, all those details apply which will be described when discussing Neradol D. The most important advantage possessed by this tanning matter, from a commercial point of view, is the lower price which it owes to the greater ease with which naphthalene may be obtained.

By treating the non-condensed crude product with barium chloride, a product completely devoid of sulphuric acid is easily obtained; the contents of sulphuric acid calculated as $BaSO_4$ is about 9.5 per cent. This value is higher than that found by Neradol D, and may be explained by the fact that a slight excess of sulphuric acid is necessary for the preparation of β-naphthalenesulphonic acid.

Comparative tanning tests using products containing sulphuric acid and products free from sulphuric acid (neutralised to the same degree of acidity) yielded leathers which were very similar; the liquor containing no sulphates yielded slightly softer leather than that obtained from a liquor containing sulphates.

An experiment was also carried out, using a liquor containing the tannin completely neutralised with caustic soda and subsequently acidified with acetic acid till the acidity of 1 gm. = 10 c.c N/10 NaOH ; here, again, no essential difference could be detected in the leather as compared with that from a liquor containing sulphates.

One of the most striking properties of this tanning matter is its solubilising effect on natural tannins and the phlobaphenes ; this property may mainly be compared to the similar one of other condensed sulphonic acids in their behaviour towards natural tannins.

If, therefore, natural tannins are mixed with this product and the solution used for tanning purposes, the resultant leather will possess a dark colour owing to the presence of solubilised phlobaphenes ; if, on the other hand, a dark coloured leather, which has been tanned with natural tannins, is washed over with a 5° Bé. solution of this synthetic tannin, or immersed for some time in the solution, the leather assumes a lighter colour owing to the phlobaphenes being dissolved and removed from the leather by the synthetic tannin.

The presence of Neradol ND in leathers is detected by methods to be described under Neradol D (cf. p. 108). The oxyazo reaction only succeeds when the solution has been boiled with a few drops of hypochlorite solution, quickly cooled and excess of ammonia added. When applying the indophenol reaction, the solution must be treated as follows : 3-4 drops of hypochlorite solution is added, and the solution heated for a short time ; or 5-6 drops hypochlorite solution may be added, and the solution left for some time, in which case the heating may be omitted. The solution is then made distinctly ammoniacal, 1-2 drops of dimethyl-*p*-phenylenediamine solution and a layer of alcohol poured on the top. In most cases a blue coloration will appear ; the addition of 1-2

drops of potassium ferricyanide solution with formation of a blue coloration indicates the presence of Neradol ND without fail.

The fact that a product possessing tanning properties may be obtained by condensing β-naphthalenesulphonic acid makes it interesting to investigate the behaviour of a non-condensed β-naphthalenesulphonic acid towards pelt. The following solutions were allowed to act upon pelt for twelve days :—

(1) Concentrated solution of α-naphthalenesulphonic acid (10° Bé.).
(2)   „   „ β-   „   „   (6° Bé.)
(3)   „   „   2, 7-   „   „   (18" Bé.).

Solution 1 swells the pelt to a considerable extent without, however, solubilising it. Solution 2 produces a similar effect. Solution 3 dissolves the pelt appreciably on the first day ; after six days, solubilisation is complete. The reason of this different behaviour of the mono- and disulphonic acids is mainly to be sought in their difference of solubility ; the monosulphonic acids are not very soluble, and are only capable of giving solutions measuring 10' and 6" Bé. respectively, whereas the disulphonic acid yields an 18" Bé. solution, in addition to which the much higher acidity of the latter quickly gelatinises the pelt.

As regards the capability of the naphthalenesulphonic acids of dissolving phlobaphenes, the following results were obtained :—solid Argentine quebracho extract was mixed with —

5 per cent. α-naphthalenesulphonic acid: opaque sol., large quantity of insolubles.
10 „   „   „   „   lesser   „   „
20 „   „   „   „   no insolubles.
30 „   „   „   „   „
5   „ β-naphthalenesulphonic acid: opaque sol., lesser quantity of insolubles.
10 „   „   „   „   „   „
20 „   „   „   „   clear solution, no insolubles.
30 „   „   „   „   „   „
5   „   2, 7-naphthalenedisulphonic acid: opaque sol., large quantity of insolubles.
10 „   2, 7   „   „   „   as above.
20 „   2, 7   „   „   slightly opaque, some insolubles.
30 „   2, 7   „   „   nearly clear solution, no insolubles.

It is hence clear that the β-sulphonic acid possesses

phlobaphene-solubilising qualities greater than those of the α-sulphonic acid or the disulphonic acid ; the β-sulphonic acid was therefore made the subject of Ger. Pat., 181,288 (8th February 1917).

The synthetic tannin, *Ordoval G*, is the formaldehyde condensation product of higher hydrocarbons (mainly *retenes*), and is a partly neutralised product containing no sulphuric acid.   The author's analysis gave the following figures :—

Tanning matters	-	-	-	10.7 per cent.
Soluble non-tannins -		-	-	16.4 ,,
Insolubles	-	-	-	0.0 ,,
Water	-	-	-	73.0 ,,

Acidity: 1 gm. = 4 c.c. N/10 NaOH.
Density: 23° Bé.

Ordoval G is completely soluble in water and glacial acetic acid.   Only its organic constituents are soluble in alcohol, ethyl acetate, and acetone, whereby a dark coloured crystalline mass separates.   Ordoval G is insoluble in benzene.

The aqueous solution of Ordoval G gives the following reactions :—

Gelatine -	-	Moderate flocculent precipitate.
Ferric chloride -	-	Darkish coloration.
Potassium dichromate -	-	No reaction.
Aniline hydrochloride -	-	Dark brown precipitate.
Formaldehyde hydrochloric acid -		No precipitate.
Bromine water -	-	No reaction.
Zinc acetate -	-	Very slight opalescence.
Barium chloride -	-	Slight opalescence.

Its capability of solubilising and consequent saving of natural tannins is shown by the fact that 100 kilos of vegetable tanning material may be substituted by 40 kilos of Ordoval G and the material in question in order to obtain the entire tanning intensity of the latter.

In one respect—that of its salts—Ordoval G differs from the Neradols ; whereas the chromium and aluminium salts of the latter possess no such tannoid properties as will make

the resultant leather exhibit any of the characteristics of either tannage, it is possible to carry out combined tannage with a mixture of Ordoval G and metallic salts. Tanning experiments carried out with the chromium, iron, aluminium, and calcium salts of Ordoval G yielded leathers which possessed proportionate characteristics of either kind of tannage to the extent to which either material was present. This combination tannage seems to be assured of a great future ; especially may a combination tannage of iron salts and Ordoval G eventually entirely replace chrome tannage.

The detection of Ordoval G in leather is carried out as follows : 10 gm. of leather are boiled with 150 c.c. of acetic acid, a solution of 25 gm. of CrO_3 in 25 c.c. of a 50 per cent. solution of acetic acid gradually added, and the mixture boiled for three hours, till the leather is decomposed and the solution has assumed a brown instead of the original light yellow colour. The solution is then evaporated, the residue dissolved in 600 c.c. hot water, and the chromium precipitated with a 40° Bé. solution of caustic soda. The solution is filtered and cooled, and a little hydrosulphite is added to 20 c.c. of the cold alkaline filtrate ; in the presence of Ordoval G, a red colour will appear (oxanthranolsulphonic acid).

Brief mention must be made of the so-called *Corinal*,[1] a synthetic tannin placed upon the market by Chem. Fabrik Worms A.-G., in Worms-on-the-Rhine. It is a viscous, brown fluid, containing the aluminium salts of the tannoid acids. The latter are formaldehyde-condensation products of sulphonated tar oils, or the hydroxylated derivatives of the latter. The density being 33° Bé., it contains 28.1 per cent. tanning matters, 13 per cent. soluble non-tannins, and 10.8 per cent. inorganic matter (3.2 per cent. Al_2O_3 and 7.6 per cent. Na_2SO_4).

A similar product, containing chrome salts as base, is the so-called **Esco-Extract**,[2] manufactured by the Chem. Fabrik Jucker & Co. in Haltingen (Baden). This product is a dark, reddish-brown fluid, possessing acid reaction, which

[1] Swiss Pat., 78,282, 78,797, 79,139.
[2] Schorlemmer, *Collegium*, 1917, 124.

strongly precipitates gelatine. Analysed by the filter method it contains 12-15 per cent. tanning matters, 17-20 per cent. soluble non-tannins, and 18 per cent. ash, of which 3 per cent. is Cr_2O_3. This synthetic tannin may be employed alone or in conjunction with other tannins, and yields a leather similar to that obtained by chrome tannage.

A. Condensation of Free Phenolsulphonic Acid

In practice, the results of condensing phenolsulphonic acid with formaldehyde are manifold, according to whether these materials are used in their concentrated or dilute state; whether they interact in the cold or when heated; or whether their interaction is gradual or rapid.

1. If a moderately dilute solution of phenolsulphonic acid (1 : 1) is mixed with one-sixth of its volume of a dilute formaldehyde solution (1 part 30 per cent. HCHO solution plus 3 parts of water) in the cold, with continuous stirring, the solution remains clear and assumes a brown colour. When left several hours, a light, white flocculent precipitate deposits, which increases in quantity on diluting with water. The solution precipitates gelatine; the flocculent precipitate is easily soluble in hot caustic soda solution, and, when subsequently neutralised with acetic acid, precipitates gelatine.

If equal parts of dilute phenolsulphonic acid and dilute formaldehyde (concentrations as above) are gradually mixed in the cold, whilst stirring, the mixture soon becomes opalescent, and a flocculent deposit separates after eighteen to twenty-four hours.

These experiments carried out on the water bath immediately yield opalescent liquids, from which an insoluble, brown, gluey, and very sticky mass separates after twenty-four hours; the latter is sparingly soluble in alkalies, partly so in organic solvents.

2. If a moderately dilute solution of phenolsulphonic acid (1 : 1) is gradually mixed with one-sixth of its volume of a concentrated (30 per cent.) formaldehyde solution in the cold, whilst stirring, slight opalescence immediately

results, and a flocculent deposit separates after about twenty minutes, which gradually increases in quantity during the next few hours. If the volume of formaldehyde is increased to the same as that of phenolsulphonic acid solution, the flocculent deposit immediately separates, and after twenty-four hours a brown, gluey, and very sticky mass—of the same solubility as that described in the previous experiment—is to be found at the bottom of the vessel used.

It should be noted that in both these experiments with concentrated formaldehyde solution a slight increase in temperature occurs concurrently with the process of condensation. If the experiments are carried out on the water bath, a gelatinous mass is instantly formed, which assumes the colours of grey, dirty light violet and dark violet, in the order named, and which, whilst left several hours—or when heated on the water bath—is suddenly converted into the insoluble, brown, gluey mass above referred to.

3. If, for the purpose of condensation, phenolsulphonic acid to which 10 per cent. of water has been added, is employed, the reaction proceeds very quickly and energetically. If one-sixth of its volume of formaldehyde (1 : 3 of the 30 per cent. solution) is added drop by drop to a cold solution of phenolsulphonic acid, a reddish, milky solution results, which assumes a slightly lighter colour on addition of more formaldehyde and deposits an insoluble flocculent precipitate. If the solution is kept below 45° C., by artificial cooling, the light colour is maintained, but a gelatinous precipitate is soon formed, the viscosity of which increases on stirring, and finally is converted into an insoluble, tough, gummy mass. If, on the other hand, the mass is heated at the beginning of the reaction, or if the amount of formaldehyde is increased and the mass cooled during reaction, effervescence occurs, and a cheesy, dirty-coloured mass results, which, on cooling, rapidly becomes solid and yields a very firm, elastic, rubbery mass, which is absolutely insoluble in water.

4. The condensation proceeds exceedingly violently when concentrated phenolsulphonic acid is acted upon by one-sixth of its volume of formaldehyde. If the latter is firstly added

drop by drop to the phenolsulphonic acid, a gel immediately results, the temperature of which quickly increases on further addition of formaldehyde and suddenly boils over, yielding a reaction product which, when cooled, forms a dirty violet, firm, elastic, and rubbery mass, insoluble in alkalies and hardly affected by organic solvents.

Finally, if the amounts of concentrated phenolsulphonic acid and formaldehyde stated above are mixed, strong effervescence occurs and heat is evolved, and a dirty blackish-violet mass is instantly formed which, on cooling, yields a rather brittle, hard product insoluble in water.

5. Totally different end-products are, however, obtained when the addition of formaldehyde (30 per cent.) in the proportion of one-sixth of the volume of dilute phenol-sulphonic acid (1 plus 9 aq.) to the latter is extended over several hours. In this case a slightly opalescent liquid is obtained which, when left twelve hours, is transformed into a brown mass soluble in water, which strongly precipitates gelatine and possesses tanning properties. Hence direct tannoid substances are obtained by this method of condensation.

Whereas no direct tanning experiment can be carried out with the insoluble compact mass obtained in the preparations described above on account of their absolute insolubility, it is still possible to carry out tanning experiments with opalescent colloidal solutions in the following ways :—

(a) If a bated pelt is immersed in a liquid containing a condensation product obtained by gradually mixing a moderately dilute solution of phenolsulphonic acid and a dilute solution of formaldehyde, the pelt is rapidly tanned on the surface. Complete penetration of the substance does not occur even after several days, since the strong acidity of the solution causes a strong swelling of the pelt.

(b) If a pelt is shaken for six hours in a shaking apparatus containing the liquid mentioned under (a), tannage again only takes place on the surface, penetration being impeded by the strong swelling effect of the liquid. Repetition of the latter two experiments, with the addition of 15 per cent. common salt, increases the tanning effect to some extent; the pelt,

however, is not tanned through, but the non-tanned layers may be clearly seen to be pickled.

The tanning effects described above are only exhibited when the colloidal tan-liquor is present in great excess over the pelt, since the former obviously only contains small amounts of tanning matter, and even the presence of common salt does not bring about complete tannage of the pelt.

In order to prove the presence of " tanning matters " in the liquid described above, several freshly prepared samples of the latter were analysed by the shake method of analysis without being first filtered and the following figures obtained:—

	1.	2.	3.	4.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Tanning matters - -	6.4	7.7	8.2	9.1
Soluble non-tannins - -	16.2	17.4	14.5	11.8

These condensation products suspended in water all precipitate gelatine strongly and leave behind a perfectly clear liquid.   In all cases, an intense blue colour was obtained on adding ferric chloride, a slight precipitate only was obtained with aniline hydrochloride, and bromine was rapidly absorbed with the separation of an insoluble white deposit.

The condensation products obtained by the interaction of dilute solutions of phenolsulphonic acid and formaldehyde at moderately high temperature, which form slimy masses and are insoluble in water, are soluble in alcohol.   An alcoholic solution of such a product was used in a tanning experiment, and a piece of pelt immersed in the solution was tanned through in a few days ; the resultant leather being rather firm, springy, and slightly hard, and the colour was a light brownish-grey.

All those condensation products which are easily or partly soluble in alcohol dissolve in caustic soda, sodium carbonate, in some cases also in borax and sodium sulphite.   They are rendered soluble with greater ease when the *freshly prepared* solution is heated on the water bath with the alkali ; the

alkaline solution, neutralised as far as is possible with acetic acid, yields light brown coloured solutions, the tanning effects of which have proved very satisfactory. Leathers tanned in such solutions, however, are rather empty and hard, possess but little resilience and an uneven, dirty greyish-brown colour.

A sample of such a product, as nearly as possible neutralised with acetic acid, contained 14.8 per cent. tanning matters, by the shake method of analysis.

B. Condensation of Partly Neutralised Phenolsulphonic Acid

Attempts were made at condensing partly neutralised phenolsulphonic acid ; the latter was obtained by mixing equal quantities of phenolsulphonic acid and sodium phenolsulphonate (prepared by exactly neutralising phenolsulphonic acid with a concentrated solution of caustic soda).

The consequent dilution and decrease in acidity, however, considerably diminished the velocity of the reaction. Hence, if the half-neutralised Solution A1 (cf. p. 98) is diluted with water, taking equal volumes, and one-sixth of the volume of dilute formaldehyde (1 : 3) gradually added in the cold, condensation is not induced. When heated several hours an opalescent liquid results from which, however, no flocculent deposits separate when left for some time. Using a concentrated solution of formaldehyde (Experiment A2, p. 98) in the cold produces no reaction, but after heating for a time an opalescent liquid is obtained. Both liquids give only slight precipitates with gelatine. Excess formaldehyde does not influence the reaction.

A repetition of Experiment A3 (cf. p. 99), using the above half-neutralised phenolsulphonic acid, similarly required heat to induce condensation, when a milky liquid of light reddish colour resulted.

Whereas the addition of formaldehyde to non neutralised concentrated phenolsulphonic acid caused violent reaction, this proceeded very slowly in the case of half-neutralised phenolsulphonic acid, resulting in the formation of a semi-

solid mass, which on heating became more viscous, and finally, when left twenty-four hours, became a solid, compact, insoluble mass possessing a dirty light violet colour.

Tanning experiments with these opalescent solutions proved them to exert a rapid penetration on the surface, complete tannage, however, taking place after eight days only, when a flat, greyish-coloured and rather hard leather resulted.

C. Condensation of Completely Neutralised Phenolsulphonic Acid

If concentrated phenolsulphonic acid is gradually neutralised with concentrated caustic soda solution till the former is faintly alkaline, the sodium salt thus obtained is not so easily condensed with formaldehyde as is the case with the free acid.

1. If formaldehyde is gradually added to the neutralised phenolsulphonic acid in the cold, opalescence immediately results; on addition of water, the liquid assumes a milky appearance. On adding gelatine to this liquid, a slimy precipitate is thrown down, leaving a slightly opalescent liquid.

2. If formaldehyde is added to neutralised phenolsulphonic acid whilst it is heated on the water bath, a slimy mass instantly separates, which on cooling solidifies and forms a greyish-blue brittle mass, insoluble in water and but sparingly soluble in alcohol; the alcoholic solution is capable of converting pelt into leather.

The filtrate from the solidified mass strongly precipitates gelatine, whereas the insoluble condensation product is soluble in caustic soda; this alkaline solution also precipitates gelatine and the addition of acetic acid transforms the mixture into the gel state.

If the insoluble condensation product is dissolved in warm concentrated sulphuric acid, the solution remains clear upon the addition of water, but does not precipitate gelatine. If, finally, this solution is neutralised with caustic soda, the solution remains clear and precipitates gelatine strongly.

D. Condensation of Cresolsulphonic Acid

Experiments were carried out with the object of condensing *o*-, *m*-, and *p*-cresolsulphonic acids with formaldehyde in various ways; no essential differences could be detected as regards the mode of reaction or the properties of the intermediary and end-products as compared to those of phenolsulphonic acid. Similarly, condensation of different samples of crude cresol containing varying quantities of *o*-, *m*-, and *p*-cresol did not yield end-products sufficiently different to justify describing them in detail.

E. Relative Behaviour of an Alkaline Solution of Bakelite and Natural Tannins

Phenolsulphonic acid was condensed with a little formaldehyde, and the reddish pasty condensation product dissolved in caustic soda. This alkaline solution of bakelite was exactly neutralised with acetic acid and mixed with strong solutions of an untreated quebracho extract. It was observed that the solubility of the quebracho extract was not increased by this treatment, but the faintly acidic character of the natural tannin caused the bakelite to be thrown down as an insoluble precipitate.

Crude phenolsulphonic acid, when added to a solution of the quebracho extract referred to, does not increase the solubility of the latter, which even deposits considerable amounts of insoluble tannin particles.

Quite different properties are exhibited by sodium phenolsulphonate, which completely converts quebracho tannin into a water-soluble substance, the aqueous solution of which deposits no insolubles. The partly neutralised condensation product of phenolsulphonic acid and formaldehyde exhibits similar properties [1] (see later).

F. Dicresylmethanedisulphonic Acid (Neradol D) [2]

Neradol D is a viscous liquid, measuring about 33° Bé., which is similar to extracts of natural tannins. One of

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[1] Grasser, *Collegium*, 1913, 521, 478.
[2] Ger. Pat., 291,457; Austr. Pat., 61,057.

its characteristics is its phenolic odour; it is completely soluble in water, forming a clear, semi-colloidal solution, but is insoluble in all organic solvents with the exception of alcohol, glacial acetic acid and ethyl acetate, which dissolve all but its inorganic constituents. The latter owe their presence to the neutralisation of the crude Neradol with caustic soda, and are composed of sodium salts of the sulphonic acid in addition to Glauber salts.

The aqueous solution of Neradol D shows properties similar to those exhibited by solutions of natural tannins and reacts as follows :—[1]

Methyl orange	-	.	-	Acid reaction.
Barium chloride	-		-	White precipitate, insoluble in HNO_3.
Ferric chloride	-		-	Deep blue coloration.
Silver nitrate	-		-	Slight opalescence.
Bromine water	-		-	No precipitate.
Formaldehyde hydrochloric acid	-			No precipitate.
Gelatine	-	.	-	Complete precipitation.
Aniline hydrochloride	-		-	Strong precipitate.

The reactions with ferric chloride and gelatine should be especially noted, since they are analogous to those given by natural tannins. On the other hand, the reactions with $BaCl_2$, bromine water and formaldehyde hydrochloric[2] acid prove the different chemical composition of Neradol D as compared to that of the natural tannins.

The fact that a positive reaction is given with aniline hydrochloride[3] is very puzzling; none of the natural tannins

[1] Grasser, *Collegium*, 1913, 520, 413.

[2] Stiasny carries out the reaction with formaldehyde-hydrochloric acid as follows :—50 c.c. of the tannin solution, plus 5 c.c. concentrated hydrochloric acid and 10 c.c. formaldehyde (40 per cent.) are heated under reflux condenser for ten minutes ; most natural tannins are completely precipitated (*Collegium*, 1906, 435 ; 1907, 52 *et* 188).

[3] This reaction is carried out as follows :—5 c.c. of the tannin solution to be examined (about 4 gm. tanning matter per litre) are shaken violently in a test tube with 0.5 c.c. aniline and 2 c.c. concentrated HCl added. All natural tannins are unaffected by this treatment, ligninsulphonic and other sulphonic acids cause opalescence. *Note.*—Employing formic acid in lieu of hydrochloric acid (Knowles) renders the reaction no more reliable.—*Transl.*

are precipitated by this reagent, but only sulphite cellulose on account of its content of ligninsulphonic acid. One is justified in assuming that there is at least some connection between the constitution of ligninsulphonic acid and that of dicresylmethanedisulphonic acid.

Stiasny[1] recommends the following reaction for the detection of and differentiation between Neradol D and wood pulp extract:—10 c.c. of a 5 per cent. solution of the extract to be analysed are violently shaken with 1-2 drops of a 1 per cent. alum solution and about 5 gm. of ammonium acetate. If only Neradol D is present no precipitate separates even after twenty-four hours, but if wood pulp be present, a precipitate is thrown down in a quantity corresponding to the amount of wood pulp present.

The official analysis gives the following figures :—[2]

Tanning matters	-	-	-	32.5	per cent.
Soluble non-tannins -		-	-	33.0	,,
Insolubles	-	-	-	0.0	,,
Water	-	-	-	34.5	,,
				100.0	per cent.
Ash -		-	-	17.0	,,

Acidity : 1 gm. = 10 c.c. N/10 NaOH.
Density : 33° Bé.

A comparison of its quantitative analysis to that of a natural tanning extract is illustrated by the following figures of a chestnut and a quebracho extract of same density (26" Bé.) :—

				Chestnut. Per Cent.	Quebracho. Per Cent.
Tanning matters		-		32.0	34.0
Soluble non-tannins		-		12.0	8.0
Insolubles	-	-	-	1.5	2.0
Water	-	-	-	54.5	56.0
				100.0	100.0
Ash	-		-	0.4	2.0

[1] *Collegium*, 1913, 516, 142.
[2] Grasser, *loc. cit.*

This comparison shows that extracts of natural tannins firstly contain certain amounts of "insolubles," whereas Neradol is completely soluble in water, forming a clear solution ; secondly, natural tanning extracts contain smaller quantities of soluble non-tannins, consisting of colouring matter and sugars, in addition to small quantities of mineral matters (ash). Neradol D contains considerable amounts of soluble non-tannins derived from salts of sulphonic and sulphuric acids, again offering a satisfactory explanation of the high ash. If, therefore, a mixture of Neradol D and a natural tanning extract was submitted to a quantitative analysis, the higher non-tannins and the high ash would indicate the presence of Neradol D, provided that wood pulp or a highly sulphited extract were not components of the mixture.

The chemical reactions taking place in the preparation of Neradol D may be expressed thus :—
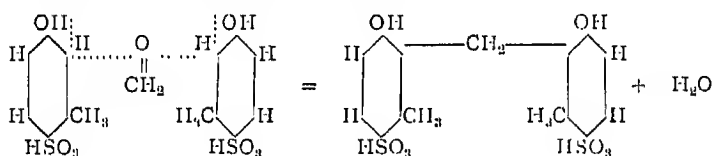
1. NERADOL D REACTIONS

1. The quantitative determination of phenols introduced by Bader,[1] which consists in precipitating them as oxyazo compounds, has been modified by Appelius and Schmidt[2] for the purpose of detecting Neradol D :—To 50 c.c. of the tannin solution (analytical strength) 15 c.c. of diazo solution are added, the mixture filtered, if necessary, and the filtrate made alkaline with caustic soda ; in the presence of Neradol D in sufficient quantity, a blood-red coloration results. If but little Neradol D be present, the procedure is altered as follows :— The tannin solution, to which the diazo solution has been added, is filtered, and the filtrate poured on a piece of filter paper which is then dried ; a solution of caustic soda is

[1] *Bull. soc. scient., Bucaresi,* 1899, 8, 51.
[2] *Collegium,* 1914, 597.

spotted on the paper, when, if Neradol D be present, a red-edged spot will appear.

According to Tschirch and Edner,[1] the diazo solution is prepared as follows:—5 gm. p-nitraniline are introduced into a 500 c.c. measuring flask, 25 c.c. of water and 6 c.c. concentrated sulphuric acid added, the mixture shaken and a solution of 3 gm. of sodium nitrite in 25 c.c. of water plus 100 c.c. of water added, and the whole then filled up to 500 c.c. The solution should be stocked in the dark.

2. A less sensitive reaction for Neradol and wood pulp extract constitutes that of Appelius and Schmidt employing cinchonine,[2] while the presence of the substances in question yields characteristic precipitates.

3. Seel and Sander[3] recommend the following method of detecting Neradol D:—

(a) *Oxyazo Reaction.*—About 5 c.c. of the tannin solution are rendered alkaline with caustic soda; after cooling with ice, about half the volume of alcohol is added. 3-4 drops of diazo solution are then added. Frequently, this results in the solution assuming a blue coloration. If not, the solution is acidified with hydrochloric acid, ether added, and the mixture well shaken. The water is now separated from the mixture, fresh water added, together with some caustic soda solution, when, if Neradol D be present, the salt of the colour acid formed dissolves in the water with a beautiful green or bluish-green colour. At the place of contact of the water and the ether a bluish-green ring appears.

The diazo solution is prepared by dissolving p-amino-phenol or its hydrochloric in a little dilute hydrochloric acid, cooling in ice and carefully diazotising in the cold till a slight excess of nitrous acid is present. It is essential that this solution should be tested before use, and this is carried out by coupling it with an alkaline phenol solution; if a dark blue oxyazo colour is formed, the solution may be used. It must be kept cool by surrounding it with ice.

(b) *Indophenol Reaction.* To 5 c.c. of the solution to be

[1] *Archiv. d. Pharm*, 1907, 150.
[2] *Collegium*, 1914, 597.
[3] *Zeits. J. ang. Chem.*, 1916, 333.

tested, a drop of a solution of dimethyl-*p*-phenylenediamine is added, the solution rendered alkaline with caustic soda and 1-2 drops of a 5 per cent. solution of potassium ferricyanide added. If Neradol D be present, a blue colour appears, either immediately or after some time. The reaction is rendered more sensitive if alcohol is carefully poured on the solution after it has been rendered alkaline, and potassium ferricyanide is then added. At the place of contact a blue layer is formed, which ultimately diffuses into the alcohol.

According to Lauffmann[1] the presence of natural tannins as well as that of wood pulp diminishes the sensitiveness of the reactions described above ;[2] this investigator recommends a modification of these reactions.

2. ELECTRO-CHEMICAL BEHAVIOUR OF NERADOL D

The author's investigations of the electro-osmosis of an aqueous solution of Neradol D[3] proved that dicresylmethanedisulphonic acid exhibits anodic migration ; hence this product possesses negative charge and acidic character. The impurities accompanying the synthetic tannin, *i.e.*, salts, free sulphuric acid, and some phenols, migrated anodic and cathodic respectively, according to their charges. A Neradol D purified by electro-osmosis finally yielded a pure solution of dicresylmethanedisulphonic acid, which precipitated gelatine and exhibited pronounced tanning effects, but gave a greenish-black coloration with iron salts. This conclusively proves that the blue coloration given by Neradol D with iron salts is no characteristic feature of the *pure* synthetic tannin, but is caused by the phenolic impurities accompanying the latter. Especially the first stage of the electro-osmosis produces a cathodic migration of the phenols, which may then be detected at a cathode by means of the iron and bromine reactions.

It is characteristic of a dicresylmethanedisulphonic acid purified by electro-osmosis that it does not precipitate aniline hydrochloride. It appears, therefore, that this reaction

[1] *Collegium*, 1917, 233.
[2] *Zeits. f. ang. Chem.*, 1916, 333.
[3] *Collegium*, 1920, 597, 24.

which is characteristic of most synthetic tannins—is again caused by the presence of impurities.

3. THE INFLUENCE OF SALTS AND ACID CONTENTS ON THE TANNING EFFECT OF NERADOL D

Chemical analysis of crude Neradol revealed a natural dicresylmethanedisulphonic acid (the tanning agent) contents of about 68 per cent., which agrees fairly well with the calculated amount. Like other "strong" and "weak" acids this sulphonic acid exercises a strongly swelling influence on pelt. Whereas the effect of acid present in solutions of Neradol D of medium concentration and its tanning effect both influence the pelt and are fairly well balanced, this is not the case as regards highly concentrated and very dilute solutions. If, for instance, a very dilute solution of crude Neradol (about 0.25° Bé.) is used, the tanning effect of this solution is exceedingly small and does not show itself till after several hours. The relatively high dissociation of the acids at this high degree of dilution causes an extremely rapid and strong swelling of the pelt, which has therefore absorbed its maximum amount of water (maximum swelling) before the tanning effect of the sulphonic acid comes into play and by fixing the surface of the pelt is enabled to prevent the excessive swelling effect of the acids.

The addition of neutral salts to the tan liquor diminishes the effect of the acids on pelt (dehydrates the pelt) and prevents "drawing" of the grain. If, for instance, common salt be added to a solution of crude Neradol, the original quantity of sulphonic acid present would remain constant, but the presence of salt would diminish the degree of dissociation and consequently the swelling. This effect is still more pronounced when the absolute amount of free sulphonic acid is diminished. Hence, if crude Neradol is treated with increasing amounts of caustic soda, a series of products containing increasing quantities of salt and decreasing concentrations of sulphonic acid is obtained.

The acidity of the Neradols may be determined by titration with N/10 caustic soda; this procedure hence establishes a

means of determining the (unknown) acidities which may be expressed in terms of c.c. N/10 NaOH. The acidity of crude Neradol was found to be—

$$1 \text{ gm.} = 50 \text{ c.c. } N/10 \text{ NaOH}$$

i.e., 1 gm. of crude Neradol requires 50 c.c. N/10 NaOH for complete neutralisation; the decrease in acidity causes a decrease in contents of tanning matters and the quantities of salts increase. The following table gives the figures obtained by differently neutralised neradols :—

Acidity.	Tanning Matters.	Na_2SO_4.
	Per Cent.	Per Cent.
1 gm. = 50 c.c.	68	...
1 ,, = 40 ,,	59	4
1 ,, = 30 ,,	50	8
1 ,, = 20 ,,	41	12
1 ,, = 10 ,,	33	17
1 ,, = 5 ,,	28	20
1 ,, = 0 ,,	20	...

Tanning experiments with these different neradols (employing solutions of 1° Bé. strength) demonstrated that neradols of acidity 50", 40°, and 30° exerted strong swelling and gave comparatively hard leathers; neradols of acidity 20", 10", and 5° exert no swelling, yield quick tannage and soft leather. The swelling (hardening) effect of the acid and the dehydrating (softening) effect of the salts in this case, therefore, are well balanced, and this fact affords an explanation of the rapid change from hardening to softening effects exhibited by partly neutralised Neradol where less acid and a greater quantity of salts respectively are present.

It may finally be noted that the acidity of Neradol D, 1 gm. = 10 c.c. N/10 NaOH, has been found to be the most suitable one for practical purposes. The author has, however, successfully employed some neradols of considerably higher acidities. The acidity above mentioned is possessed by a Neradol D containing 17 per cent. ash and 30 per cent.

sodium sulphonates and Glauber's salts crystals respectively. This large quantity of salts present on the one hand effects the rapid pickle and tanning effect exhibited by Neradol D, on the other hand it also effects the softness in the leather resulting from its use either alone or in admixture with natural tannins.

4. Philobaphene-Solubilising Action of Neradols

A special feature of Neradol D is its property of solubilising phlobaphenes, which may be ascribed to its contents of sulphonic acids or their salts. In order to demonstrate whether the sulphonic acids and their salts are capable of solubilising the insoluble or sparingly soluble anhydrides of the tannins (the phlobaphenes) before and after condensation, the following experiments were carried out :—

Crude Argentine solid quebracho extract was converted into a highly viscous liquid by treating it for several hours with water at 100° C., and the anhydrides rendered insoluble by diluting the liquid with a large volume of cold water. The precipitate formed, consisting of quebracho phlobaphenes, was separated from the liquid by decantation, and purified by washing it several times with water. Each 10 gm. of this moist paste were treated in the cold with (a) free phenolsulphonic acid ; (b) sodium phenolsulphonate ; (c) crude Neradol and (d) Neradol D, 20 c.c. of water at 45° C. added, and the mixture allowed to cool slowly ; the following solutions resulted :—

(a) Opalescent solution, much deposit.
(b) Clear solution, no deposit.
(c) Nearly clear solution, very little deposit.
(d) Clear solution, no deposit.

This clearly proves that free and condensed phenolsulphonic acids as such are not capable of completely solubilising phlobaphenes, whereas the sodium salts of free and condensed phenolsulphonic acids possess this property. The salt contents of Neradol D, therefore, constitute an advantage in this respect, that not only may Neradol D be mixed with solutions of any natural tannin without insolubles

being thereby deposited, but it may also be added in large quantities to a tannin solution with the result that the sparingly soluble and wholly insoluble constituents (phlobaphenes) are completely brought into solution.

The practical importance of the solubilising effect of Neradol D relating to solid Argentine quebracho extract is demonstrated in the following series of investigations carried out by the author :—[1]

Solid Argentine Quebracho Extract.	Neradol D.	Matters Calc.	Tanning of Mixture Found.	Abs. Increase in Tanning Matters.	Increase per 100 gms. Extract.
Gm.	Gm.	Per Cent.		Per Cent.	
100	0	66.0	66.0	...	...
0	100	32.5	32.5	...	...
90	10	62.7	64.7	2.0	2.2
80	20	56.1	58.7	2.6	3.3
60	40	52.6	56.9	4.3	7.1
50	50	49.3	55.2	5.9	11.8
30	70	42.6	47.3	4.7	15.6
20	80	39.2	42.3	3.1	15.5

The maximum solubilising effect is exhibited in the mixture of 70 parts of Neradol and 30 parts of quebracho, with an additional percentage of tanning matters in the mixture of 15.6 per cent.—a figure which is very nearly identical with that of the insolubles present in the original Argentine quebracho extract.

The phlobaphene-solubilising property of Neradol D is closely connected with the influence of the latter on the colour of leathers tanned with natural tannins. If, on the one hand, a pelt is tanned with natural (i.e., non-treated) quebracho extract, a rather light coloured leather results, the fleshy colour of which is characteristic of quebracho. The dark coloured phlobaphenes present, on account of their insolubility, will have no influence on the colour of the leather. If, now, the quebracho extract be treated with sulphite and bisulphite in the usual way, the phlobaphenes are solubilised, but the reducing effect of the bisulphite

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[1] *Collegium*, 1913, 478 ; Austr. Pat., 68,796.

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tends to brighten the colour of the otherwise dark coloured phlobaphenes as well as that of the soluble tannins, and a reddish-yellow coloured extract results, imparting its own colour to the pelt. When, on the other hand, the quebracho extract is solubilised by means of Neradol D, the phlobaphenes are brought into solution without reduction taking place, and a dark brownish-red extract results, which imparts a similar colour to the finished leather. This darkening effect of Neradol D is most conspicuous in the case of mangrove, maletto, and chestnut, but is absent in the case of algarobilla, dividivi, gambir, sumac, and valonea. The varying phlobaphene contents of the tannins easily afford an explanation of the different properties above alluded to : the mangrove phlobaphenes are dark coloured bodies, those of mimosa, maletto, and chestnut are of lighter colour, and the last-named tanning materials enumerated above are either devoid of phlobaphenes or possess them only as very light coloured bodies. Algarobilla, sumac, gambir, dividivi, and valonea, on the other hand, are associated with large amounts of sparingly soluble ellagic acid, known as " bloom " or " mud," which imparts a light colour to the finished leather, and conveniently covers the dark colour imparted to the leather by other tanning materials ; for this reason the former are often used in the lay-aways or in the finishing processes.

Similar effects to those of Neradol D are exhibited by other salts of sulphonic acids, e.g., sodium benzylsulphanilate (Solvenol B.A.S.F., or solution salt ("Solutionsalz") Hoechst); the author prepared mixtures of such salts and untreated quebracho extract in order to determine their solubilising effects, and arrived at the following results :—

30 parts Solvenol plus 70 parts quebracho extract ; clear solution, no deposit.
25	,,	,,	25	,,	,,	clear solution, very little deposit
20	,,	,,	80	,,	,,	nearly clear solution, very little deposit
15	,,	,,	85	,,	,,	slightly opaque solution, some deposit.

Leathers tanned with these mixtures were more or less

dark coloured according to the amounts used of solvenol and the consequent solubilisation of the phlobaphenes.

A similar effect, though of opposite nature from a tanning standpoint, is exhibited by sulphonates on certain colloidal dark coloured substances. A phenolsulphonic acid, which had been overheated during sulphonation and subsequently condensed (crude Neradol), imparted a conspicuous greyish-brown colour to the leather; samples of this crude product were then partly neutralised with varying amounts of alkali, and these samples (containing increasing quantities of salts) tested for tannin and colour effects. It was found that the more highly neutralised samples imparted a darker colour to the solutions, but these dark products did not deposit the dark impurities on the pelt. One may therefore assume that tannoid substances are colloidally suspended, and when converted into true solutions are incapable of being fixed in insoluble form by the pelt.

Just as, by adding Neradol D to a tanning extract, the phlobaphenes are solubilised and a dark coloured extract results, it is also possible to remove the mechanically deposited phlobaphenes and oxidised tannins from the finished leather, and, as a consequence, lighten the colour of the leather. For practical purposes, bleaching with Neradol D is carried out by brushing over the darkly coloured leather with a 2°-3° Bé. solution of Neradol D, and then rinsing well with water, in order to remove the solubilised tannin. A lighter colour may also be obtained by immersing the leather in a liquor of the strength mentioned above for several hours, and then rinsing with water, but by this procedure not only the surface tannin is removed, but also tannin from the leather substance itself; this method is therefore not suitable for heavy leathers which are sold by weight.

The advantage of employing Neradol D as a bleach in this way is to be found in the fact that, on the one hand, the bleaching sulphonic acid attacks the leather to a much slighter extent than is the case with inorganic acids usually employed for this purpose; on the other hand, the method of brushing the sulphonic acid on the leather only introduces small amounts of sulphonic acid in the leather, thus lessening

the harmful effects of acids upon leather. Furthermore, the common methods of using alkalies as tannin-solubilising agents with the consequent running off and waste of alkaline tan liquors are here substituted by a method leaving liquors rich in tannin and Neradol, and which may be used in the ordinary procedure of tannage.

Since Neradol D contains neutral sodium sulphate (about 3 per cent.), and the latter, by precipitating colouring matters present in tan liquors, may slightly bleach these, it was of interest to determine whether the sodium sulphate plays any part in the bleaching effected by Neradol. Mixtures of chestnut and quebracho extracts were prepared, to which were added :—

(1) 5 per cent. Neradol D.
(2)   „   „   free from Na_2SO_4.
(3) 0.15 per cent. sodium sulphate (corresponding to above Neradol D).

These mixtures were allowed to act upon pelt alongside of comparison tests using quebracho and chestnut extracts only, the strength of the liquors in all cases being 1.5" Bé.; the pelt was left in the solution till tanned through. The following results were obtained :—

(1) Quebracho tanned leather was darker; no difference in colour by chestnut extract.
(2) Similar to (1).
(3) Same colour as given by the original extracts.

This experiment demonstrates that absence of sodium sulphate in the mixture is without influence on the colour of the resulting leather, and that an addition of sodium sulphate to natural extracts does not affect the colour imparted by them to pelt.

5. EFFECT OF NERADOL D ON PELT

Being a sulphonic acid derivative, the chemical constitution of Neradol is obviously considerably different from that of the natural tannins, and the question has been asked : Will

Neradol D, in its concentrated form, attack the hide sub-
stance?[1]   Bearing in mind that concentrated extracts of
vegetable tannins in some circumstances effect a "dead"
tannage (cf. case-hardening) and hence reduce their practical
value, and that for this reason it is impossible to allow either
concentrated extracts or concentrated Neradol D to act upon
pelt, the author still decided to carry out some experiments
in this direction. Concentrated Neradol D (33° Bé.) and
strong aqueous solutions of this material in strengths of—

$$30° \quad 25° \quad 20° \quad 15° \quad 10° \quad 5° \quad 3° \quad 1° \text{ Bé.}$$

were therefore allowed to remain in contact with pelt for a
period of ten days, when the pelts were taken out and washed
in running water for twenty-four hours, and then dried.   The
resultant leathers possessed the following properties :—

33' Bé. solution : completely gelatinised.[2]
30°   „   „   „   [2]
25°   „   two-thirds gelatinised ; surface tanned.
20°   „   one third gelatinised ; surface "dead" tanned.
15°   „   pelt was glassy throughout.
10°   „   rather cracky leather, but well tanned.
 5°   „   normal tannage.
 3'   „   „   „
 1'   „   „   „

The interiors of the leathers obtained from the 25   and
20' Bé. solutions were completely gelatinised ; this may be
accounted for by assuming that the surface was "dead"
tanned, and that hence the free dissociated sulphonic acid
diffused into the leather, towards which it exhibited hydro-
lysing rather than a tannoid effect with the consequent result
described above.   Above 10' Bé. the effect is more that of an
acid with concentrations below 10' Bé.—the only ones of tech-
nical importance—however, no ill-effects may be observed

For tanning purposes, Neradol D solutions of 2 Bé. are

[1] *Collegium*, 1913, 521, 487
[2] It was impossible to subject the pieces to a proper washing out

quite satisfactory, and it has been found [1] that solutions of this strength do not dissolve out any protein of the hide. [2]

A purely Neradol D tanned leather may be produced by immersing a bated pelt, free from lime, in a 2° Bé. Neradol D liquor for about four days ; the resultant leather being nearly white and otherwise very similar to a leather tanned with vegetable tanning materials.

The main application of Neradol D is in admixture with vegetable tanning materials ; especially in the early stages of tannage is this substance of value, since by its use not only a light coloured leather surface is obtained, but its presence prevents a subsequent dead tannage when strong vegetable tan liquors are applied, and it also imparts strength to the grain layer. It is thus possible to shorten the time consumed by the tanning process by employing Neradol D in the manner described.

A further explanation as to why the tanning process is considerably hastened by using Neradol D, either alone or in conjunction with natural tannins, is afforded by the fact that though Neradol D quickly penetrates the grain, it is but "loosely" fixed by the latter, *i.e.*, it is not deposited to such an extent that it would prevent penetration of the vegetable tannins. In the case of a mixture of Neradol D and vegetable tannins, the former quickly diffuses into the pelt and fixes the fibres, thus facilitating penetration of the vegetable tannins. This assumption is justified in view of the speed with which Neradol D completely penetrates and tans the pelt, since Neradol D containing acids and salts exhibits effects similar to those of a pickle.

6. REACTIONS OF NERADOL D WITH IRON AND ALKALIES

A special characteristic of Neradol D tannage is the sensitiveness of the latter to the action of iron and alkalies. The active principle of Neradol D being free dicresylmethanedisul-

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[1] *Technikum*, 1913, 80, 324

[2] The translator cannot agree with the author on this point. He has, for instance, found that solutions of analytical strength dissolve considerable amounts of hide substance, and his practical experience confirms results arrived at in the laboratory.

phonic acid, which is easily neutralised by lime, ammonia, and amino-acids and hence rendered inactive for tanning purposes, it is essential that the pelt prior to tannage with Neradol D should be completely delimed, bated, and freed from all constituents possessing alkaline reaction. It is, however, possible to regenerate Neradol D liquors contaminated with alkali or partly neutralised by the addition of small quantities of organic (formic, acetic, lactic, and butyric) or inorganic (hydrochloric or sulphuric) acids, i.e., the dicresyl-methanedisulphonic acid is again partly liberated, and this procedure is always preferred where the tanning process does not allow of a complete deliming of the pelt prior to intro-ducing the latter into a Neradol D liquor. If, on the other hand, such liquors are kept properly, and the addition of acid referred to kept up, they will remain active for weeks and need only strengthening up with the requisite quantity of Neradol prior to introducing fresh pack.

The sensitiveness to alkalies of Neradol D is considerably greater than in the case of natural tannins, and it appears that a vegetable tan liquor neutralised with lime will not even surface-tan when acting upon pelt and will neither impart a dark colour to the leather nor remove from it any appreciable amount of protein. Similarly, a Neradol D liquor neutralised with lime exerts no tanning action, but in contradistinction to the vegetable tan liquor similarly treated, will impart a blue or blackish-blue colour to the pelt, from which it removes larger quantities of protein. The author examined two such liquors relating to their contents of tanning matters and protein and obtained the following results :—

	Reaction.	Barl	Tans.	Non tans	Insol	Pro teins.
				Per Cent	Per Cent	Per Cent	Per Cent
Vegetable tan liquor	Slightly alkaline	12	0	2 03	0, 35	0 01
Neradol		,,	,,	10'	0	4 43	0, 17	0, 17

These figures do not only show the higher protein contents of the Neradol D liquor, but do also show higher contents in soluble non-tannins, which consist mainly of lime (2.12 per

cent.) and sodium salts (1.8 per cent.), thus establishing the fact of the sensitiveness of Neradol D to alkalies in addition to its lime-solubilising effects.

The sensitiveness towards alkalies is also noticeable on a large scale where the tanpits have been built of cement; though the pelt may be quite free from lime, the Neradol D is quickly neutralised by the cement, with results similar to those enumerated above.

The blue coloured soluble compound of Neradol D and iron salts, to which frequent reference has been made, is very important from a practical standpoint. Whereas the catechol tannins (i.e., fir, gambir, hemlock, cutch, mangrove, and quebracho) are coloured black, those of the pyrogallol class (i.e., algarobilla, dividivi, valonea, gallotannic acid, myrabolams, and sumac) bluish-black, and the "mixed" tannins (i.e., canaigre, oak, and mimosa bark) bluish-purple by iron alum, Neradol D is coloured a pure blue. How sensitive this reaction is, the following comparative analyses illustrate: to each litre of tan liquor containing 4 gm. tanning matter prepared from (a) quebracho extract and (b) Neradol D, 10 c.c. of a 10 per cent. iron alum solution were added, the solutions heated to 100° C., cooled and filtered, and the colour of the filtrates and the weight of the precipitates determined :—

(a) Quebracho solution : light reddish-brown filtrate, 3.22 gm. precipitate.

(b) Neradol solution : deep blue filtrate, 0.02 gm. precipitate.

Hence, on adding a soluble iron salt to a solution of a natural tannin, most of the tanning matter is precipitated; the colour of the filtrate, however, is much the same as that of the original solution. A Neradol D liquor similarly treated gives no precipitate, but is coloured blue throughout. The filtrates from the above solutions were allowed to act upon pelt, and the following observations were made : –

(a) The light reddish-brown filtrate from the quebracho liquor exhibited no well-defined tanning effect on pelt, to which it imparted a light brown colour.

(b) On the other hand, the deep blue filtrate from the Neradol D liquor exhibited well-defined tanning effects, and imparted a deep blue colour to the pelt.

For practical purposes, the sensitiveness of Neradol D to iron is not only remarkable because any contact with iron particles will colour the liquor (and hence the pelt) blue, but also because the slight amount of iron always present in cement renders the use of cement pits prohibitive where Neradol D liquors are used.

This intense blue coloration might have made possible a colorimetric estimation of Neradol D. The author has investigated this possibility, using different concentrations of Neradol D liquors to which a solution of iron ammonium alum was added, and found that when, at certain concentrations, the maximum blue colour had been obtained, it was still possible to increase the quantity of Neradol without the intensity of the colour being affected. Addition of a little alkali tends at first to darken the blue colour, more alkali changes the blue colour to brown and yellow, successive additions of a weak organic acid (*e.g.*, acetic acid) rapidly lighten the blue colour. Since industrially used Neradol D liquors always contain varying quantities of acid and may be neutral or even slightly alkaline, it must be considered impossible to make any use of such a colorimetric estimation for practical purposes.

7. REAGENTS SUITABLE FOR DEMONSTRATING THE VARIOUS STAGES OF NERADOL D TANNAGE

The extent to which tannage with Neradol D proceeds on the surface and within the pelt may be judged from the feel of the skin, but such a method is totally unsuited to any but a practical tanner. A suitable and reliable reagent is indigotine (B.A.S.F), which clearly distinguishes tanned and untanned layers of the pelt. If, for instance, a 1-2 per cent. solution of indigotine is brought into contact with a fresh cut on a pelt, and the latter subsequently washed with warm water, the indigotine is only retained by the untanned parts, a leather tanned with Neradol D is therefore only coloured by indigotine to the extent to which it has combined with the Neradol [1]

[1] According to Seel and Sander (*Zeits f ang Chem.*, 1916, 333), basic dyestuffs are also very suitable for demonstrating tanned parts of the pelt

Another reagent is constituted by iron ammonium sulphate; the extent of the penetration of Neradol D, which gives an intense blue coloration with iron salts, into the leather may be determined by washing the pelt treated with Neradol D, making a cut, again washing and treating the cut with a few drops of a weak solution of iron ammonium sulphate. Those parts of the pelt which have been converted into leather then appear deep blue; on the other hand, those which have been in contact with Neradol D, but have not yet been converted into leather, are light blue. Those parts which have not yet been in contact with Neradol D appear pure white; the results of this reaction are therefore opposite to those obtained by the use of indigotine.

8. Combination Tannages with Neradol D

Whereas mixtures of Neradol D and vegetable tannins impart properties to the leather consistent with the proportions in which these materials are present, it is not possible to combine Neradol D with mineral tanning agents or fats (*e.g.*, fish oils, etc.) in such a way that a leather characterised by the properties of either material is obtained. Experiments were carried out using (1) chrome salts plus Neradol D; (2) aluminium salts plus Neradol D; and (3) oils plus Neradol D, and the following conclusions were arrived at:—

1. **Chrome-Neradol D** liquors, containing comparatively larger amounts of Neradol D, act too rapidly on the pelt and draw the grain; smaller amounts of Neradol D seem without influence on the finished leather, which possesses pronounced characteristics of chrome leather. Another disagreeable factor is the following: the chrome salts must possess a certain degree of basicity in order to produce good leather; the Neradol D must, on the other hand, possess a certain acidity to produce the optimum results, and it is hence impossible to balance practically the basicity of the chrome salts and the acidity of the Neradol in order to justify the presence of both. If one of the two is used separately before the other, a leather always results possessing the characteristics of the material first employed, provided the time of action has been sufficiently

extended. If insufficient time has been allowed, the characteristics imparted by the main tanning agent are not altered.

2. **Aluminium Salts and Neradol** require practically the same basicity and acidity respectively, and when combined always yield a leather possessing mainly the properties of one of the components. In addition to this fact, leathers tanned with aluminium salts possess great softness and stretch, those tanned with Neradol D greater firmness and less stretch, and these opposing qualities completely compensate one another and render *nil* the value of such mixtures.

In addition to this, the presence of aluminium salts produces no better fixation on the leather fibre of basic coal-tar dyes, so that in this respect also a combination of aluminium salts and Neradol D is of no value.

3. Just as aluminium salts impart special characteristics to leather, this property is exhibited by fatty matters, especially so as regards stretchiness and softness. Both of the latter are not apparent to the same extent in an oil tannage into which Neradol D and oil enter as constituents. It is, however, not excluded that, in view of the fact that the combination of oils and Neradol D appear to produce the most promising results of the three from a technical point of view, such combination would yield products possessing less stretch and greater softness which, by occupying an intermediary position, might possess certain advantages and be useful for certain technical purposes.

9. Analysis of Leather containing Neradol D

Chemical examination of leathers tanned with Neradol D or with mixtures of natural tannins and Neradol D often involve a determination of the materials employed in tannage. In most leathers exclusively tanned with vegetable tanning materials, it is usually possible to determine at least the nature of the main tanning agent, whereas the attempts at determining those tannins which are only present in minor quantities rarely succeed. Since Neradol D usually is employed in comparatively small quantities, it has been imperative to find

a method which also permits of the detection of smaller quantities of Neradol D. Provided the presence of not less than 5 per cent. (on the weight of the leather) of Neradol D, the following method yields reliable results:—20-30 gm. of the leather are ground or sliced as finely as possible and the powder (or the slices) treated in the cold with a sufficient volume of dilute ammonia solution (5 c.c. ammonia plus 95 c.c. of water) for eight to twelve hours. The object of this is to dissolve the tannins, but no protein should go into solution. The solution is filtered and the filtrate evaporated on the water bath till it occupies a volume of about 30 c.c. A few c.c. of aniline hydrochloride are now cautiously added, when it should be carefully noted if a precipitate is thrown down which might be either completely or only partly soluble in excess of aniline hydrochloride. A precipitate is always thrown down when Neradol D or wood pulp is present; only the Neradol D precipitate is soluble in excess of aniline hydrochloride. Partial solubility of the precipitate therefore indicates the presence of both wood pulp and Neradol D.

The quantitative determination of sulphuric acid—the detection and estimation of which in leather is important—is considerably influenced by the presence of Neradol D. Practically all methods in vogue dealing with its determination were based on the estimation of the sulphur introduced into leather by sulphuric acid. The presence of Neradol D, the main constituent of which is dicresylmethanedisulphonic acid, renders it impossible by such methods to determine whether the combined sulphur owes its origin to sulphuric or sulphonic acid. It remains yet to be determined whether the sulphonic acid influences the leather substance to the extent that sulphuric acid does; it must, however, be borne in mind that Neradol D in addition to free sulphonic acid also contains sulphonates and sulphates, which may enter into the leather and thus increase the sulphur contents of the latter. A method must hence be devised which estimates the free acid only and provides the means of distinguishing this from all other acids of organic and inorganic acids. Paessler,[1] by extracting the

[1] Collegium, 1914, 527, 126; 531, 509; 532, 567

leather and dialysing the filtrate, has effected a separation of the acids and the tanning and colouring matters and quantitatively estimated the sulphuric acid in the dialysate.

Immerheiser [1] devised a method, based upon the property of sulphuric acid of combining with ether, for the purpose of determining free sulphuric acid in leathers:—10 gm. of the leather, cut into small pieces, are extracted three times with 200 c.c. distilled water at room temperature, the time of each extraction being ten to twelve hours, and the combined extracts evaporated to dryness on the water bath, 5 gm. of quartz sand being added. The dry residue is now powdered, introduced into an Erlenmeyer flask provided with a glass stopper, and 200 c.c. of anhydrous ether [2] added. After about two hours, during which the flask is occasionally shaken, the ether is poured through a filter, the residue washed with a little ether, and the operation repeated twice with each 40 c.c. anhydrous ether, using the same filter. To the combined ether extracts (about 200 c.c.) HCl and $BaCl_2$ are added, the ether distilled off and the residue evaporated on the water bath, in order to decompose the ether-sulphuric acid compound. 50 c.c. of hot water acidified with HCl are now added, the precipitate allowed to settle, filtered, washed, dried, and weighed. The sulphuric acid thus estimated was present in the leather as *free sulphuric acid*. That present as sulphates soluble in water is estimated in the residue on the filter. the residue is extracted with hot water, the sand filtered off, the filtrate acidified with HCl, boiled for one quarter hour and filtered if necessary The clear filtrate, which may be coloured, is brought to boil and $BaCl_2$ is added. The barium sulphate indicates the sulphuric acid present in the leather as watersoluble sulphates.

Whether the latter be sulphates or bisulphates may be indicated by the aqueous extract of the above residue, since neutral reaction would indicate the absence of bisulphates, acid reaction their presence in addition to possible normal sulphates, the quantitative estimation of the metals would decide this point definitely.

[1] *Collegium*, 1918, 582, 293.
[2] To be tested for water by shaking with anhydrous copper sulphate.

10. PROPERTIES OF LEATHERS TANNED WITH NERADOL D

Whereas the colour of leathers tanned with Neradol D only is nearly a pure white, those tanned with mixtures of Neradol D and vegetable tanning materials are more or less light coloured according to the quantity of Neradol D present, as has been explained when discussing the phlobaphene-solubilising action of Neradol D. In any case, all leathers tanned with Neradol D possess fibre of remarkable length, which explains their increased tensile strength and elasticity. The tensile strength of a leather tanned with a mixture of Neradol D and vegetable tannins was 3.7 per cent. as compared to 3 per cent. when no Neradol was used; the extension was 56 per cent. when tanning with Neradol D as against 36 per cent. without the latter.

The sensitiveness to light of leathers tanned with Neradol D may be mentioned. Exposed to direct sunlight, the surface of the leather assumes a yellowish colour after two days' exposure, and assumes a pure yellow colour after a further three days. A further fifteen days' exposure only darkens the leather slightly, the final colour being very little different from the one obtaining after five days' exposure.

In passing, it may be remarked that this yellow colour is observed on the surface only, the grain otherwise possessing that pure white colour characteristic of Neradol D tanned leather. Further, it may be noted that leathers tanned with Neradol D fix basic coal-tar dyes excellently, whereas acid and substantive dyestuffs are fixed with other than their natural shades.

The author has analysed a leather exclusively tanned with Neradol D, and has obtained the following results : - [1]

Moisture -	15 53	per cent.
Ash	0 93	,,
Fats -	1 26	,,
Extraneous matters -	0 00	,,
Leather { Tanning matters -	36 92	,,
substance { Hide substance -	15 36	,,

100 00 per cent.

Sp. gr., 0.642.

[1] *Collegium*, 1913, 521, 478.

From these figures, those of "degree of tannage" and "yield" (pelt——→leather) are calculated as 81.4 and 220 respectively.

These figures correspond closely to those obtained by the analysis of leathers tanned with vegetable tanning materials, and this proves the similarity between the Neradol D tannage and a vegetable tannage in their chemical aspects.

11. NERADOL D FREE FROM SULPHURIC ACID

In order to prepare phenol and cresulphonic acids, such quantities of technical sulphuric acid are used as do not allow of the assumption of complete utilisation of the sulphuric acid ; hence it was of theoretical interest to remove eventual traces of free sulphuric acid from the product. For this purpose, the author diluted crude Neradol to 20° Bé. and gradually added small quantities of milk of lime ; the precipitates were freed from the liquid by suction and washing, and a Neradol free from sulphuric acid resulted, which was then brought to the acidity of Neradol D with the calculated amount of alkali. From the calcium sulphate precipitate, the amount of sulphuric acid originally present was calculated, and was found to be only 4 per cent.

The acid-free sample of Neradol was tested with regard to its suitability as a tanning agent ; leather tanned with this sample differed from one tanned with an untreated sample (Neradol D) by being harder and possessing a pronouncedly greyish colour. This difference, however, may not be due to the absence of sulphuric acid but to the presence of the slightly soluble calcium sulphate in the sample treated with milk of lime To prove this point, another way of preparing Neradol D free from sulphuric acid was looked out for. Sodium acetate was added to a solution of crude Neradol until the latter was no longer acid to congo-red ; at this point no free sulphuric acid can be present in the solution. The product, partly neutralised till the acidity of Neradol D was reached (part of the acidity then being due to liberated acetic acid), yielded a leather which neither in colour nor in feel differed from the usual Neradol D tanned leather. This proves that the grey colour and the hardness of the leather

described in the former experiment is due to the presence of calcium sulphate.

If the crude Neradol treated with sodium acetate is not partly neutralised, the analysis gives the following figures :—

Tanning matters	-	-	-	67.3 per cent.
Soluble non-tannins	-	-	-	8.6 ,,
Insolubles	-	-	-	0.0 ,,
Water	-	-	-	24.1 ,,

100.0 per cent.

Acidity : 1 gm. = 46 c.c. N/10 NaOH.

Compared to the analysis of crude Neradol containing sulphuric acid, the figures show that, on the one hand, the presence of the comparatively small quantity of sodium acetate but slightly influences the contents of non-tannins and water, but, on the other hand, reduces the contents of tannins and also the acidity. The tanning intensity of this product, however, is considerably increased, and using a 1° Bé. solution a leather is obtained in a very short time very similar to that yielded by ordinary Neradol D, but considerably harder ; the latter property is due to higher acidity and almost complete absence of salts in the product treated with sodium acetate.

The author finally attempted to partly neutralise crude Neradol with various hydroxides and carried out tanning tests with samples containing the different metals. Hardly any difference in the finished leathers could be observed as regards colour or quality ; the tannage could by no means be described as that of a combination of Neradol D and the respective metals

12. NEUTRAL NERADOL

Crude Neradol, completely neutralised with caustic soda, yields a product of the following composition · —

Tanning matters	-		19 8 per cent.
Soluble non-tannins	-		37.9 ,,
Insolubles	-	-	0.0 ,,
Water	-	-	42.3 ,,

100 0 per cent

The qualitative reactions of this product differ from those of non-neutralised Neradol to the extent that gelatine is not precipitated and iron salts are not coloured blue, but dirty brown, by the aqueous solution of this product.

The completely neutralised product, diluted to various concentrations (of 1°, 2°, 3°, and 5° Bé.) and tested as to tanning properties, revealed the surprising fact that the pelts were not even surface tanned, and were coloured evenly blue throughout by indigotine.

It might have been anticipated that sodium dicresyl-methanedisulphonate would be as devoid of tanning powers as is a neutralised vegetable tannin, but it is difficult to explain the fact of the sodium salt being adsorbed by hide powder as "tanning matters" in the Official Method of Analysis. Brought to a logical conclusion, the figure 19.8 per cent. should be deducted from 32.5 per cent. obtained in the analysis of a *partly* neutralised Neradol D, which comparatively large quantities of the sodium sulphonate also adsorbed by hide powder, leaving the "tanning matters" of Neradol D at 13.5 per cent.

This diminished figure, however, does in no way reduce the value as a tanning agent of Neradol D; it merely shows how inadequate is the hide powder method of analysis when applied to substances of the composition of Neradol D. This is further confirmed by the Loewenthal permanganate method, which yields the following figures :—

Tanning matters	-	-	-	7 2	per cent.
Soluble non-tannins -		-	-	59 2 [1]	,,

If, on the other hand, completely neutralised Neradol is acidified with an organic acid, such as acetic acid, till the acidity (1 gm. = 10 c c. N/10 NaOH) is reached, the resulting product is in all respects similar to Neradol D and yields a corresponding leather.

It is permissible to assume that the irregularity exhibited by Neradol D as regards the analytical estimation of its tannin contents is connected with the low molecular weight of the tanning principle. Whereas all tannins so far isolated from

[1] *Collegium*, 1913, 521, 487.

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the natural tanning materials possess rather high molecular weights, that of Neradol D deviates considerably from this rule, as is shown by the following table :—

Neradol D tannin		-	-	$C_{15}H_{16}S_2O_8$	-	-	358
Mangrove	,,	-	-	$C_{21}H_{40}O_{21}$	-	-	670
Oak bark	,,	-	-	$C_{28}H_{20}O_{23}$	-	-	840
Myrabolam	,,	-	-	$C_{51}H_{48}O_{85}$	-	-	1256
Dividivi	,,	-	-	$C_{51}H_{10}O_{86}$	-	-	1270
Malletto	,,	-	-	$(C_{41}H_{50}O_{20})_2$	-	-	1724

This low molecular weight may mainly account for the figures obtained by the incorrect oxymetric estimation with permanganate ; the apparent tannoid property of the tannoid-inactive neutral salt of dicresylmethanedisulphonic acid may be explained by assuming that though it is, probably, in the colloidal state, and as such adsorbed by hide powder, it is still devoid of astringent properties.

G. Different Methods of Condensation as Applied to Phenolsulphonic Acid

In addition to formaldehyde, many other substances may, theoretically, induce condensation of phenolsulphonic acid ; condensation takes place either with the elimination of water or, in addition to this, with the introduction of methane group.

So far, the following condensing agents have been investigated :—

(1) Heating *in vacuo*.
(2) Sulphur chloride.
(3) Phosphorus compounds.
(4) Aldehydes.
(5) Glycerol

1. Condensation Induced by Heat

If phenolsulphonic acid is heated *in vacuo* at 130° C. for twenty hours, condensation takes place [1] without the addition

[1] Austr. Pat., 64,479

of any condensing agent, and an anhydride of the composition
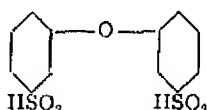
is formed. This product is a viscous liquid, possessing a very corrosive action. Added to a solution of gelatine, a light, fine flocculent precipitate is thrown down. Analysed by the shake method of analysis, the tannin content of the product equals about 46 per cent. Its strongly acidic and hence swelling character does not express qualities consistent with the conception of suitability for tanning purposes: a sample of the product was therefore partly neutralised to the acidity of Neradol D, when the shake method of analysis yielded the following figures :—

Tanning matters	-	-	21.5 per cent.
Soluble non-tannins	-	-	48.3 ,,
Water	-	-	30.2 ,,
			100.0 per cent.

This partly neutralised sulphonic acid represents a white, pasty mass, which is not particularly easily soluble in water, yielding a solution of milky appearance. Treated with the usual tannin reagents, it exhibits the following characteristics:—

Gelatine	- Light flocculent precipitate
Bromine water	- Complete fixation.
Ferric chloride	- Cherry-red coloration
Lead acetate	- Very slight precipitate, insoluble HNO_3.
Aniline hydrochloride	- Slight precipitate.

Solutions of this product in concentrations from 1°-8 Bé. exerted no tanning action whatever, whereas more concentrated solutions (15° Bé.) converted pelt in eight days into a leather very similar to a Neradol D leather in colour and feel, but considerably harder.

In order to determine its phlobaphene-solubilising effects, samples of the product were mixed with concentrated quebracho extract in the proportions 5, 10, 20, and 30 per cent. on the

weight of extract, and the following observations made :—
5 and 10 per cent. were without effect, 20 and 30 per cent.
showed some solubilising tendency, but on diluting the mixture
with water the quebracho was completely thrown out of
solution. Apparently this anhydride is, in this respect also,
quite different from the partly neutralised diphenylmethane-
disulphonic acid.

2. Condensation with Sulphur Chloride

When sulphur chloride is allowed to act upon phenol-
sulphonic acid whilst heat is applied, a yellowish-grey mass
results, which dissolves in water, forming a reddish-yellow
solution. Neutralised to acidity 10, it exhibits the following
reactions :—

Gelatine	- Precipitate.
Ferric chloride -	- Deep blue coloration.
Lead acetate -	- White precipitate, insoluble HNO_3.
Aniline hydrochloride -	- Precipitate.
Bromine water -	- No reaction.

The partly neutralised 2° Bé. solution of this product
yielded a reddish-grey coloured leather, the qualities of which
were very similar to that yielded by Neradol D.

3. Condensation with Phosphorus Compounds

Schiff's well-known synthesis,[1] in which phosphorus
oxychloride interacts with phenolsulphonic acid, yields a
product which exhibits some tannin reactions, but which,
when acting on pelt, converts the latter into a leather which,
when dried, is very cracky. If, on the other hand, cresol-
sulphonic acid is condensed with phosphorus oxychloride by
heating the two together, products eminently suitable for
tanning purposes result. These products are non-crystalline
bodies easily soluble in water, and are coloured bluish-violet
by ferric chloride and precipitate gelatine. Solutions of the

[1] Liebig's *Ann*, 178, 173

free acids and acidified solutions of the salts convert pelt into firm and white leathers possessing great softness and pliability.[1]

4. CONDENSATION WITH ALDEHYDES

By treating phenolsulphonic acid with acetaldehyde in the usual way, a viscous brown mass is obtained, which is very soluble in water, the solution being of a brown colour. When brought to acidity 10, the following reactions are exhibited by the product :—

Gelatine - -	- Precipitate.
Ferric chloride - -	- Deep blue coloration.
Aqueous ammonia -	- Cherry-red coloration.
Lead acetate - -	- Yellowish precipitate, insoluble HNO_3.
Aniline hydrochloride -	- Yellow precipitate, soluble excess aniline.
Bromine water - -	- No reaction.

Tanning experiments with this substance yielded, even after extended tannage, an undertanned leather, the surfaces being coloured brown, the inner layers, however, white. Further neutralisation reduces the tanning intensity of the product ; the addition of sodium sulphate to the original partly neutralised product hastened tannage, the leather, however, possessing dark colour and being undertanned. The following constitution may be ascribed to this product :—

OII   OII

—CH_2——CH_2—

HSO_3 HSO_3
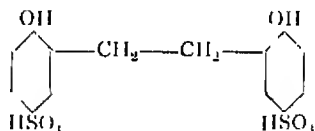
If benzaldehyde is used in lieu of acetaldehyde for condensing phenolsulphonic acid, a water-soluble product results, exhibiting reactions similar to those of the acetaldehyde-condensation product. The former product is more suitable

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[1] Austr. Pat., 66,895.

as a tanning agent and yields a reddish-brown rather firm and hard leather; it possesses the constitution—
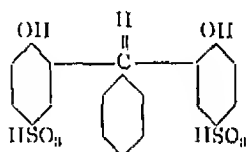
For the purpose of condensing phenol with formaldehyde, it is not essential to first convert the phenol into the water-soluble phenolsulphonic acid, since it is possible to convert the condensation products of phenol and its derivatives, which are soluble in alkali, into water-soluble form by either heating the condensation products with concentrated solutions of formaldehyde and neutral sulphites, or by dissolving the condensation products in alkali and inducing reaction by means of formaldehyde bisulphite.[1] Highly concentrated solutions result, which may be concentrated either as such or after the alkali present has been neutralised. The sulphurous acid formed prevents oxidation of the product on evaporation. A special advantage of this method of preparation is the fact that sulphuric acid, which is but difficultly removed from the end-product, is not employed at all.

The product thus obtained is a yellowish-white crumbly mass, which is very soluble in water, forming a clear solution. The latter exhibits the following reactions:—

Gelatine - -	Precipitate.
Ferric chloride -	Deep blue coloration.
Aqueous ammonia	- Cherry-red coloration.
Lead acetate -	White precipitate, insoluble in HNO_3.
Aniline hydrochloride	Precipitate
Bromine water -	No reaction.

The product brought to acidity 10, yielded on analysis the following figures:—

[1] *Collegium*, 1913, 518, 324.

Tanning matters	-	-	-	25.2 per cent.
Soluble non-tannins -		-	-	56.5 ,,
Insolubles	-	-	-	0.0 ,,
Water	-	-	-	18.3 ,,

100.0 per cent.

Tanning experiments with this substance yielded white and soft leathers, which were indistinguishable from those tanned with Neradol D.

A characteristic feature of this synthetic tannin is its behaviour in concentrated form towards pelt, which is not attacked by it, but is readily tanned even at such high concentrations. An explanation of this is to be found in the large quantity of salts present in the product. A disadvantage of this synthetic tannin is its complete incapability of dissolving phlobaphenes, which is even so far extended as to precipitate otherwise easily soluble tannins when adding it to solutions of the latter in comparatively large proportions ; here, again, the salts are responsible for this behaviour, their large quantities effecting a salting out of the natural tannins.

The class of aldehyde condensations also comprises that of inducing condensation by means of sugars ; if phenol-sulphonic acid is heated with glucose, a reddish-brown liquid results, which is soluble in water. The solution exhibits reactions similar to those of Neradol D. It is, however, not possible, by this method of condensation, to prepare as highly concentrated products as is possible in the case of Neradol D, since employing sugars as condensation agents means liberation of a large volume of water. Analysis of this product, using the shake method, gives a tannin content of 16.2 per cent. ; tanning experiments demonstrated that the time of tannage, using a 2 Bé. solution, was the same as that required by Neradol D, and yielded a leather, the surface of which was reddish-grey, the inner layers being white, but which is otherwise very similar to Neradol D tanned leather.[1]

Relatively to its capability of solubilising phlobaphenes, this product exhibits similar properties to that obtained by

[1] Austr Pat , 69,375, 69,376, 69,377.

merely heating phenolsulphonic acid, to a slight extent
only solubilising quebracho extract, which, on diluting the
mixture, is completely thrown out of solution.

5. CONDENSATION WITH GLYCEROL .

Phenolsulphonic acid, when heated with glycerol, undergoes
the process of condensation, and forms a brown fluid, which,
when brought to acidity to, exhibits the following reactions :—

Gelatine -	Precipitate.
Ferric chloride	- Brown black coloration.
Lead acetate -	- White precipitate, insoluble in HNO_3.
Aniline hydrochloride	Slight precipitate.

Tanning experiments with this partly neutralised product
resulted in a very gradual conversion of the pelt into a
greenish grey coloured leather ; the colour, however, does not
penetrate the pelt and is hence caused by colloidally suspended
impurities   If the solution is filtered through a filter candle,
a somewhat clearer solution results, but the latter also tans
very slowly and yields a brown coloured leather.

Analyses of the partly neutralised product reveals a tannin
content of 17.6 per cent. A 2° Bé solution of the non-
neutralised product showed a rapid tanning effect at first, when
brought into contact with pelt, on which it had a strong
swelling effect, and to which it imparted a greenish colour ;
the tanning effect, however, slowed down considerably, after a
few days, and the solution penetrated the pelt only very
gradually ; this is probably due to the presence of large
quantities of colloidally suspended impurities, which, when the
substance is partly neutralised with the formation of salts of
the sulphonic acids, are brought into true solution and hence
penetrate the pelt with greater rapidity

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